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LIQUID PROPELLANTS SYMPOSIUM (U)
27-28 March 1957

Sponsored by
Technical Advisory Panel on Fuels and Lubricants
OFFICE OF THE ASSISTANT SECRETARY OF DEFENSE
RESEARCH AND DEVELOPMENT

SPECIAL HANDLING REQUIRED
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F O R E W O R D

The Liquid Propellants Symposium, held 27-28 March 1957, was sponsored by the Technical Advisory Panel on Fuels and Lubricants, of the Office of the Assistant Secretary of Defense (Research and Development). The technical content of the Symposium was selected by an ad hoc Papers Review Committee with the following membership:

PAPERS REVIEW COMMITTEE

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Mr. Oscar Bessio, Bureau of Aeronautics (Navy)

Dr. H. W. Carhart, Naval Research Laboratory

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Commander R. C. Truax, Western Development Division,
    Air Research and Development Command

Dr. J. G. Tschinkel, Army Ballistic Missile Agency

Mr. B. F. Wilkes, Hq, U. S. Air Force

Twenty-two papers were presented at the symposium, nineteen of which were included in Volume 1, PFL 212/13, Liquid Propellants Symposium. The other three are included in this volume. In addition, sixteen papers were read by title only at the symposium. Thirteen of the latter papers were included in Volume 2, PFL 212/13, Liquid Propellants Symposium, and the other three are included in this volume.

Also included in this volume is prepared discussion on eighteen papers and general floor discussion. Each discusser has been

given an opportunity to edit the transcript of his discussion before inclusion.

A total of 747 persons were cleared for attendance at the symposium. The 500 who attended represented 152 industrial and educational organizations and numerous military agencies.

Donald B. Brooks
Secretary, Technical Advisory
Panel on Fuels and Lubricants

C O N T E N T S

*   *   *   *

27 MARCH 1957
MORNING SESSION

CHAIRMAN: DR. NOAH S. DAVIS, JR.

DR. DAVIS: Good morning, ladies and gentlemen. I have the pleasure of presenting Mr. Holaday, Deputy Assistant Secretary of Defense, who will give the "Welcome."

MR. W. M. HOLADAY, OASD (R&E): Ladies and gentlemen, it is my privilege to welcome you to this symposium.

I believe all of you realize that I am a very strong supporter of symposiums, because I think they furnish a needed means of communication. We have been trying to sponsor more symposiums, particularly in the areas where new work is developing and new people wish to get into the activity. This is the second symposium I have attended recently. In some of them, of course, we do not have as large a group as this. I think you may be interested in knowing we have seven hundred fifty people registered for this meeting, of whom about 500 are present.

I am sure you all realize that a great deal of effort goes into the preparation of these symposiums. Our advisory panels first point out the need for them. The panels are of great assistance in helping to get the right papers and people to present them for the interest of all of you.

Incidentally, our advisory panels are made up of industry representatives who work with us to keep us informed of the latest work that is going on in industry. The panels also provide us with an opportunity to tell the industry representatives the problems that are confronting the Department of Defense. Thus we have a two-way flow of information through our panels. We can't have everyone represented, of course, but we do try to get a good cross section of industry.

The staff of our Technical Advisory Panel on Fuels and Lubricants has been responsible for organizing this symposium. They have received valuable technical help in planning the meeting and selecting the papers, from representatives of the Services and from industry, especially from the Papers Review Committee.

We are very glad you could come today. We think that the exchange of information on industry problems and Services problems will be of mutual benefit. However, to give you a little broader view of the over-all work, we have asked Mr. Murphree, the Special Assistant for Guided Missiles, to give you a short outline of our over-all problem. At this time I would like to introduce Mr. Murphree to you.

MR. E. V. MURPHREE, ASSISTANT TO THE SECRETARY OF DEFENSE FOR GUIDED MISSILES: I would like to add my welcome to that of Bill Holaday's, and to point out to you the importance of this symposium and of the weapons programs to which it is directed.

I know many of you are familiar in general, and maybe in considerable detail, with the guided missile field, which is one of the primary consumers of liquid propellants. I think, however, I would like to touch again on the importance of guided missiles and to point out what a profound change they are going to make and are making in our weapons systems, and to do that we might look at some of the missile categories.

If we consider first the long-range surface-to-surface missiles such as the IRBM of 1500 miles range, or the ICBM of 5500 or so miles, these types of weapons are bound in time to replace the use of manned bombers for many long-range bombing missions.

The reason for this is that they are less vulnerable to enemy attack and destruction and so they have a better chance of getting to the target and delivering their warhead than is the case of manned bombers, and this greater chance is going to increase as the enemy defenses against manned planes are built up.

Also these long-range surface-to-surface missiles take less manpower for given delivery capability than manned bombers and in addition their investment is lower, so you will get more striking power per dollar.

Now, to offset this to some extent, I don't think in the present state of the art that one could say that long-range surface-to-surface missiles would be suitable weapons against concentrated small area hard targets. They are good weapons against industrial areas and things of that kind, or anti-aircraft defense complexes; but against individual hard targets they probably won't have the accuracy, at least for a considerable time, to be the right weapon to use against that sort of target. I think one might picture that you might use long-range missiles in a softening-up operation and then use manned bombers to go after the hard targets.

Now, a second category of guided missiles is the surface-to-air missiles. These missiles are playing today an important major part in our air defense and their importance will grow with time. If there are adequate numbers of surface-to-air missile installations, one can

get a very tight defense for vital areas and these missiles are very effective. Those under advanced development will be very effective against all types of planes and the slower surface-to-surface and air-to-surface missiles.

For this purpose in time they will replace short-range manned interceptors. The trend is for missiles to go out in range. One of the real limitations in range of guided missiles now is the range of acquisition and target trading radars. As the range of these types of radars is increased, the range of missiles will make a corresponding gain.

I think we can look for a steady development in the direction of greater range for surface-to-air guided missiles. I think at the same time we should realize we have not solved air defense problems. Present surface-to-air missiles will offer no defense at the present time, nor will any missile in a very active phase of development offer any defense against ballistic missiles or the faster types of air-breathing surface-to-surface or air-to-surface missiles. That has to be another step in this country's development.

A third classification of missiles is air-to-air missiles. The purpose of these missiles is to make manned interceptor planes more effective. Since the last war the speed of manned bombers has been increasing and there has not been a corresponding increase in the range of our acquisition methods -- that is, acquisition radars -- and as a result of this there has been a growing decrease in the time available to make the interception. The purpose of these air-to-air missiles carried by planes is to be sure that in the short time available for interception, that interception will be effective.

Manned interceptors are probably going to stay in our weapons picture for quite a long time. They can go out farther than guided missiles can, and they can cover areas where there are no adequate surface-to-air missile defenses.

The last general classification of guided missiles is the air-to-surface missiles. These missiles are to be carried by planes to be delivered at a target some distance away.

We are building up a fleet of quite modern bombing planes that are going to be with us for quite a while, and we want to be sure that these planes are as effective as possible. In time it seems likely against strongly-defended areas a manned plane is going to have a very difficult time in getting through due to surface-to-air missile defenses that will be built up. So for the attack to be effective, the idea has been evolved of having these air-to-surface missiles so that the plane can stand out some distance from the strongly-defended area and launch missiles against the areas as a target.

As I mentioned, the missile field is probably the primary field to which liquid propellants are directed, and I think you can see from what I have said that this area is very essential to our national defense. Any advance in liquid propellants or fuels will have a most important bearing on this country's defense effectiveness.

There are other military applications of rockets which are quite important and various other developments are foreseen in which we will use rocket power.

From this background it seems to be particularly fitting that this symposium on liquid propellants be held to give a picture of the present state of the art and the direction of possible advances. We have been fortunate in having today a very representative gathering with; first, the Federal Government represented by several government bureaus and the three branches of the Armed Services; second, the chemical, petroleum, and processing industries; third, designers and developers of rocket power plants; fourth, designers and developers of complete missiles systems; and fifth, active representatives of academic and other research institutions. These groups are the ones who, through their collected efforts, can make real forward steps in getting better weapons through advances in liquid propellants.

This symposium has been designed for the purpose of giving a picture of the present state of the art, as I mentioned before, and possible directions of future advances. I would expect much cross-fertilization in the development of new ideas in and from the discussions that you hold here in the next two days. I think we might look at the direction some of these developments may take. It seems to me we have two broad needs.

One is with our present types of liquid propellants we want to know how we can improve performance and reliability of those types through control of composition and other properties. Some of the papers of this symposium are directed to that subject. Second, for new liquid propellants we would like to be able to develop much superior properties, and this development must involve a number of things which have to be balanced in future developments. One of the things, of course, that one desires most is greater specific impulse. This, however, has to be coupled with ease of handling and use and ability to be stable during long storage periods. Also we would like propellants that have less requirements for logistics support, and they should, of course, have adequate reliability and a cost that is not excessive for their use.

I don't want to emphasize the cost too much. The rocket field can stand expensive fuels if they really give high performance, and I think you would have to use this cost in quite a relative sense.

With the present types of propellants we are using and which we will be using for a considerable distance ahead, it is quite

4

important that we know just what types of propellants of the present
kind will give the best performance. I think the only way that is
really going to be answered effectively is the same way that questions
on fuels for air-breathing arrangements are answered; that is, you have
to try them out in the use for which they are intended and really find
what compositions and types give the best performance and what can be
done to improve that performance.

Now, looking at improved liquid propellants of a newer type
than those presently available, as I mentioned earlier, the thing we
probably want most of all is greater specific impulse. This has the
advantage that it has the possibility of offering greater range. If
we are not interested in greater range we can get greater pay load;
and finally, for the same range and same pay load we can get greater
mobility because the missile will be smaller and weigh less; so those
are the advantages that high specific impulse offers.

I tried to get some examples to make the advantages of
specific impulse a little more concrete. The figures I got seemed
to me to be a little too optimistic in added range; maybe they weren't,
but I prefer not to use them. I can assure you, however, that you can
get some very real advantages out of fuels of higher specific impulse,
provided they have other desirable properties.

We know, for example, that fluorine and hydrogen, or
fluorine-ammonia, as well as some other materials, will give consider-
ably higher specific impulse. However, they have other problems. One
of our present propellants is jet fuel and liquid oxygen, and we have
a lot of trouble handling liquid oxygen and particularly its use does
not look attractive in combat areas. Liquid fluorine indeed looks
less attractive from a handling standpoint than liquid oxygen, and so
it would be desirable to have propellants that would give high specific
impulse but don't have so many other problems associated with them.
That does not mean that we are not interested in liquid fluorine as
a liquid propellant, because we are. But we would also be interested
in easy ones to handle.

I should point out that liquid propellants are getting a
lot of competition from solid propellants. This is particularly true
for the shorter-range missiles, and this trend is extending as far in
range as toward the IRBM, which is a missile of some 1500 miles in
range. It is unlikely that the trend will go to as long range as
the ICBM of somewhat over 5000 miles.

The reasons for this trend are that solid propellants com-
pared with liquid propellants at the present time offer; first, a
greater state of readiness as they are ready to go without much pre-
liminary adjustment or check; second, their motor is less complicated;
third, there are no moving parts; and fourth, they have greater
reliability at the present time and they have no logistic problems
like handling liquid oxygen, for example, under combat conditions.

The objection to solid propellants is that they are relatively low in specific impulse compared to liquid propellants, and hence particularly for larger and longer range missiles this means greater weight or loss in mobility. This trend for solid propellants to take over the liquid propellants field for certain types of missiles should be a real challenge to this symposium.

For quite short-range missiles I don't believe that liquid propellants as now foreseen can in general compete with solid propellants. They should be in the running, however, for medium-range missiles. In order for them to improve their position we will have to develop liquid propellants that are easier to handle than the present ones and at the same time will be stable for a long period.

This, to me, is the primary job for the research and later development groups. We also need greater mechanical reliability and the greater state of readiness for liquid propellant motors. This is a job for the liquid propellant motor people and the missiles systems people in general. We also need to take full advantage of the higher specific impulse that liquid propellants offer and this again is a job, I think, for the rocket engine people and the missiles systems people.

I would like to close by saying that I feel this symposium is a very excellent idea. Through your suggestions at the symposium and the thoughts and information you will take with you from the symposium, I am looking forward to seeing in time some really worth-while new developments.

I am glad to have this opportunity to be with you. Thank you.

PAPER

THE EFFECT OF PROPELLANT ENERGY AND MASS DISTRIBUTION ON ROCKET PROPULSION EFFICIENCY

by Howard S. Seifert
The Ramo-Wooldridge Corporation

PREPARED DISCUSSION

None

GENERAL DISCUSSION

None

PAPER

AN EVALUATION OF LIQUID OZONE-OXYGEN MIXTURES AS ROCKET OXIDIZERS

by J. P. Layton, J. Glassman, D. Smith.
Princeton University

PREPARED DISCUSSION

by G. M. Platz
Armour Research Foundation

Discussion Prepared by
G. M. Platz
Armour Research Foundation
Chicago 16, Illinois

on J. P. Layton, I. Glassman, D. Garvin Paper
AN EVALUATION OF LIQUID OZONE-OXYGEN MIXTURES AS ROCKET OXIDIZERS

The program just described by Mr. Layton represents the first bonafide attempt to "reduce to practice" the utilization of liquid ozone as a rocket propellant. This program had been preceded by several years of research by:

(1) The Linde Air Products Company which studied the physical properties and sensitivity of liquid ozone
(2) The Welsbach Corporation which studied the requirements for tonnage production of liquid ozone
(3) The Air Reduction Company which studied both the production and handling of liquid ozone
(4) The Armour Research Foundation which studied the production, stabilization, physical properties, and handling of liquid ozone

Despite this extensive research, many areas of uncertainty still remain. These, coupled with the discouraging reports of neophytes in the field of ozone technology, prompted The James Forrestal Research Center to lay out a program which would more clearly predict the proper course of investigation at a maximum of safety to project personnel. JFRC realized at the very beginning that if this material could not be handled with a reasonable degree of safety in an installation such as theirs, field utilization was impossible. Therefore they made every attempt to "play it safe" - a policy which, from the standpoint of personnel safety, has paid off.

The only criticism which I can make of their program from a technical standpoint, is that some portions of their installation have suffered from overdesign while other portions of the equipment seem to suffer from the converse.

Mr. Layton has pointed out several areas where further research and development are needed for more rapid progress. I agree with him on these points and would like to add one more for future use. Namely, the development of a facility to be used for the training of both military and contractor personnel should this oxidizer become feasible at a later date.

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GENERAL DISCUSSION

MR. LOUIS RAPP (Hughes Tool Company, Aircraft Division):
I would like to ask Pres just one question. I came approximately 3000
miles to attend this meeting. I would like to have, if possible, just
a little bit of a hint as to whether or not any performance was ob-
tained from this work. Did you get 95%, or 90%, or what percent of
theoretical?

MR. LAYTON: Louis, from what we know so far, I have no
reason to believe that we will not get what we expect to get.

PAPER

HYDROGEN PEROXIDE PROPELLANTS

by Andrew J. Kubica & John H. Keefe
(Presented by Mr. Keefe)
Becco Chemical Division of
Food Machinery & Chemical Corporation

(See pages 30 to 64, Volume 1, PYL 222/13)

PREPARED DISCUSSION

by R. J. Thompson
Rocketdyne

(See following pages, 10-13)

Discussion Prepared by
Dr. R. J. Thompson
Rocketdyne
Canoga Park, California

on Andrew J. Kubica and John H. Keefe Paper
HYDROGEN PEROXIDE PROPELLANTS

The authors are to be commended on their very able present-
ation of recent research findings on hydrogen peroxide. We at
Rocketdyne certainly concur with them in their enthusiasm for hydro-
gen peroxide as an outstanding oxidizer for a variety of liquid
propellant rocket applications. We should like to offer a few com-
ments from the point of view of the engine development agency in
order to stimulate further interest and thinking on this versatile
oxidant.

As the authors have indicated, a large part of the current
interest in hydrogen peroxide is for bipropellant rocket application
in manned aircraft. Use of peroxide in aircraft goes back, of
course, to the German rocket interceptor planes of World War II and
has also been quite extensively exploited in Great Britain. In the
applications currently under development, advantage is taken of the
excellent ignition and combustion characteristics of peroxide with
the aircraft jet engine fuel, so that a separate rocket fuel system
is required. The authors have discussed the thermal ignition system
based on initial exothermic decomposition of the oxidizer and post-
injection of fuel. This makes for a highly reliable and quite simple
engine capable of repetitive operation. Since full oxidizer decom-
position is assured before fuel entry, the risk of explosive mal-
function is minimized, and complex, precisely timed sequential
controls are avoided. At the same time, monopropellant decomposi-
tion of peroxide provides clean, consistent quality turbine drive
gas at a convenient temperature in a very simple manner. Another
obvious advantage is the ease of varying thrust over about a two to
one range by throttling the fuel only. This combination of oper-
ational advantages, together with generally satisfactory physical
properties and a specific impulse at least as good as that of other
storable oxidizers makes hydrogen peroxide particularly well suited
to the aircraft superperformance operation.

In a manned aircraft application, considerations of safety in storage and handling, as well as in the engine, are paramount. The work done by Becco over the past several years has assisted greatly in allaying fears as to the hazards involved in large-scale use of hydrogen peroxide. Rocketdyne has stored, handled and decomposed many tons of high-strength hydrogen peroxide in the 75- to 90-percent concentration range, both at our Field Test Laboratory and at several government test sites. These operations are now quite routine. We believe that hydrogen peroxide must always be treated with healthy respect, including use of appropriate materials and properly designed equipment, thorough training of personnel and scrupulous cleanliness to avoid organic or catalytic contaminants. With these precautions, it is no more hazardous than many chemicals commonly employed in industry. Fortunately, hydrogen peroxide can always be rendered innocuous simply by dilution with water.

Now I would like to comment in somewhat more detail on certain points in Kubica and Keefe's paper. The authors present the physical properties of the various hydrogen peroxide propellants at essentially ambient conditions, with extrapolation of heat capacity data to higher temperatures by correlation techniques. In order to carry out fluid flow and heat transfer calculation under rocket conditions, the designer has a real need for accurate physical property data at elevated temperatures and pressures, up to about 500 F and 700 or 800 psi. Use of theoretical correlations to extrapolate from the near ambient experimental data may lead to significant errors. Properties of interest include density, viscosity, heat capacity and thermal conductivity. Rocketdyne is now measuring these properties. One has to work rather quickly because of the greatly accelerated thermal decomposition rate at high temperatures, but it appears that quite accurate results will be obtained up to at least 400 F.

Becco's work on low-freezing hydrogen peroxide propellants is of great interest. The high freezing point of 90-percent hydrogen peroxide is clearly a disadvantage in some applications, although its significance has perhaps been somewhat exaggerated in comparison with the many favorable characteristics of hydrogen peroxide. The ingenious device by means of which the heat of decomposition of a small part of the hydrogen peroxide is used to warm the bulk liquid should be developed to the point of practical application. We believe that insofar as possible the hydrogen peroxide freezing problem should be dealt with by the exercise of engineering ingenuity, of which this device is an example, in order to retain the advantages of highly purified 90- to 100-percent hydrogen peroxide in stability, performance and extensive development experience. However, it is encouraging to know that such good progress is also being made on the chemical additive approach.

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The feasibility of regenerative cooling with 90-percent hydrogen peroxide is now thoroughly established; regeneratively cooled hydrogen peroxide-jet fuel engines are being produced and tested in a routine manner. Research is under way to establish the limits of hydrogen peroxide cooling capabilities, but no practical problems in this area are foreseen. However, as the authors have indicated, further work is required to establish, unambiguously, the limits of shock and confinement under which hydrogen peroxides of various concentrations can propagate detonation. While the authors are probably correct in stating that the mechanical shock and adiabatic compression sensitivity are too low to constitute an operational hazard, we cannot agree that the complete absence of hazard has yet been conclusively proven. One area of ignorance not discussed by the authors is the combined effect of elevated temperature and pressure on the explosive concentration limit of hydrogen peroxide vapor. Existing data are inadequate for reliable extrapolation of the vapor explosion limit to high pressure.

One dilemma in hydrogen peroxide development has been the desire for both excellent storage stability and excellent catalytic decomposition on demand. Both storage stability and catalyst behavior have been greatly improved by the fine work of the hydrogen peroxide manufacturers in producing a product of the highest purity. Stabilizers are well known which could make 90-percent hydrogen peroxide suitable for protracted storage in sealed vessels and tolerant of some degree of accidental contamination. Unfortunately, these stabilizers exert an adverse effect on catalyst activity or life, or both, so that the engine catalyst pack must be larger and be renewed more often, both disadvantages in an aircraft application. One attractive solution to this dilemma is the use of thermal rather than catalytic decomposition, perhaps with a small catalytic "pilot" flame, as suggested by the authors. As concentrations increase from 90 percent toward 100 percent, the increased heat release makes thermal decomposition more attractive. However, major design effort will be required to attain a rate-of-throughput with a thermal decomposer equal to that now attained in the catalytic decomposer. This research and development effort is being initiated at Rocketdyne.

Finally, the authors have touched on the performance advantage of 100-percent hydrogen peroxide. The increased specific impulse is particularly important for higher performance of large ballistic missiles. The 100-percent hydrogen peroxide also exhibits better storage stability and, as mentioned above, may be suitable for thermal decomposition with little or no catalyst. Rocketdyne is very enthusiastic about the potential of this material. Further testing is required to establish how much, if any, increase in detonation hazard occurs as the 100-percent concentration is approached.

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It should be noted that the improvement in specific impulse with concentration of hydrogen peroxide in the 90- to 100-percent range is nonlinear; for example, an increase in concentration to 95 percent, which should not appreciably increase operational hazard, yields 70 percent of the available impulse gain, and each percent of water removed thereafter yields relatively less performance increase. It is expected that 95- to 100-percent hydrogen peroxide will be under active research testing in gas generators and bi-propellant thrust chambers at Rocketdyne within the next few months.

GENERAL DISCUSSION

D. M. KALLAS (Material Laboratory, New York Naval Shipyard, Brooklyn, New York): This statement is classified Confidential. We have no preconceived notions about the behavior of hydrogen peroxide and we treat it with a lot of respect in the work that we have done with regard to fire-fighting techniques on mixtures of hydrogen peroxide and JP-5 fuels. Some of our experiences -- and they are based on preliminary tests only which I hope will not give you any preconceived notions either -- are based on experiments in which we impinge a high-pressure jet of water onto a mixture of hydrogen peroxide and JP-5 fuel in an open container. We expected this to cause detonations. So far, we have not gotten such detonations. And I am making these remarks in connection with the effects of mechanical impact of mechanical forces on these mixtures. We are continuing these tests because we are still wondering whether we will get such an effect. Possibly it is the dilution of hydrogen peroxide that is preventing detonations.

VOICE: I'm just wondering how you can mix hydrogen peroxide and kerosene.

MR. KALLAS: We mixed those and did not get any detonations when we mixed them.

VOICE: How can you mix them if they are not miscible?

MR. KALLAS: They are not miscible; that's true. By mixing I have meant that we dump them both into an open container.

VOICE: Then you had layers?

MR. KALLAS: That is correct.

MORRIS ROSENTHAL (Radioplane Company): Mr. Thompson mentioned the word "stabilizers" for hydrogen peroxide which would permit stowage in steel containers for a short length of time, but which result in ignition difficulties at present. What I would like to know from Mr. Thompson is, does he have any information on the permissible length of stowage time, and also whether the ignition problem is solely one of difficulty on re-ignition and restarting?

DR. THOMPSON: I can say something on that. John Keefe may want to comment also. The chief experience on highly stabilized peroxide is on the 70% material, which is used in Navy torpedoes. This is heavily stabilized with sodium stannate and, I believe, sodium phosphate to the point where it can be kept in a sealed torpedo for a long time.

As torpedoes don't have the space and weight limitations of a missile or aircraft, a larger catalyst bed is used with much lower fuel input in pounds per square inch per second. A considerably larger

anti-catalyst effect by the stabilizer can thus be tolerated. However, the standard silver screen catalyst which is being used with 90% peroxide for Navy applications will tolerate almost any inorganic impurity in terms of both fast starting -- that is, getting up to full pressure in a fraction of a second -- and in catalyst life.

MR. KEEFE: There has been quite a bit of work done on stabilizers for hydrogen peroxide by the Naval Underwater Ordnance Station and by Massachusetts Institute of Technology. Commercial hydrogen peroxide solutions up to 50 weight percent are quite heavily stabilized. The 90% material sold today is stabilized to a slight extent -- that is, it contains about two milligrams of tin per liter. This is added as a conditioner or stabilizer.

Any material that will remain behind in a catalyst bed will eventually cause plugging. We think that the sulphate at 3.25 parts per million acts simply as a mechanical plugging agent. A high tin content might not poison the catalyst but might plug the bed. If you are interested in long catalyst life, you have to keep the stabilizer content low. If you are interested in one-shot applications such as torpedoes, stabilizers certainly can be used. The torpedo is not sealed up tight during storage on the submarine or destroyer. There is a vent valve which is closed prior to firing.

W. C. ROEGGERATH (Lockheed Aircraft Corporation): Is there any test evidence available about regenerative cooling with 100% hydrogen peroxide?

MR. KEEFE: I know of no actual tests where 100% H_2O_2 has been used for regenerative cooling. I don't believe it has been tried as yet.

MR. ROSENTHAL: Inasmuch as the Armed Services are represented, I wonder if any of them have any comments about the pros and cons of using hydrogen peroxide as a propellant in service applications.

W. R. FISH (Naval Ordnance Test Station): In our work on the LAR we have considered it absolutely necessary to seal the rocket completely. This and the requirement for meeting a -65° freezing point have eliminated the use of peroxide.

I wonder if Mr. Keefe is aware of the work done earlier at NOTS on solutions of ammonium nitrate and water in peroxide that did actually meet our freezing point requirement but did not meet the stability requirement.

This leaves for us -- and I will discuss this more tomorrow afternoon -- only red acid as a possible oxidizer, because this material can be sealed up and stowed in the rocket for long periods of time. One of our objects is to load the rocket at the time of assembly, stow

the rocket sealed up for periods as long as five years, and this is the basis for our objection or our inability to use peroxide.

MR. KEEFE: Yes, we are aware of the work that NOTS did earlier. We have your reports and have found them very valuable.

We have worked with ammonium nitrate/hydrogen peroxide/water solution having a -65°F freezing point. However, this has a relatively low impulse with JP-4 of about 190 seconds at 20 to 1 expansion ratio.

PAPER

PERFORMANCE OF PERCHLORYL FLUORIDE

by E. A. Mickel, K. Berman, E. S. C. Gantz
(Presented by Dr. Gantz)
General Electric Company

(See pages 65 to 75, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by W. P. Knight
Aerojet-General Corporation

(See following pages, 17-22)

CONFIDENTIAL

Discussion Prepared by
W. P. Knight
Aerojet-General Corporation
Azusa, California

on E. A. Mickle, K. Berman, and E. S. C. Gantz Paper
PERFORMANCE OF PERCHLORYL FLUORIDE

I. **INTRODUCTION**

    A. In the short period of time since perchloryl fluoride has be-
come available in at least research quantities, interest in this new
oxidizer for potential use in rockets has oscillated considerably. It is
only natural that extreme interest should be exhibited in a material with
as high an oxidizing potential and yet as tractable as perchloryl fluoride.
It is believed that the lessening of interest in this compound is caused
by the same characteristic that has prevented the wide spread use of
liquid ammonia in rocket engines; that is, the high vapor pressure with
its attendant requirements for high pressure systems with subsequent
weight penalties.

    B. The first use of perchloryl fluoride as an oxidizer for rocket
engines was made at the Naval Air Rocket Test Station (references 1 & 2).
Here it was shown, not in laboratory tests but in rocket hardware, to be
a material of relatively easy handling characteristics, low corrosivity,
and smooth combustion properties. The toxicity, as reported by the Penn-
sylvania Salt Manufacturing Co., is low.

    C. Other than the tests at NARTS, there has been a lack of informa-
tion concerning the use of perchloryl fluoride in rocket hardware. The
information presented by the General Electric Co. therefore is of extreme
interest and the data concerning the high combustion efficiency is
welcomed.

II. **PERFORMANCE CALCULATIONS**

    A. As soon as the value for the heat of formation of perchloryl
fluoride had been established, the Aerojet-General Corporation also calcu-
lated the theoretical specific impulse for unsym.-dimethylhydrazine with
perchloryl fluoride. These calculations were performed for a chamber
pressure of 300 psia, an exhaust pressure of one atmosphere, and under

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conditions of shifting equilibrium. The results indicated an optimum mixture ratio of 2.55 which yielded an I_{sp} of 256 lb-sec/lb. These values agree very closely with the data reported by General Electric.

B.   Aerojet has also calculated the performance of ethyldecaborane with perchloryl fluoride under the same conditions as for the calculations above. Table I was prepared to illustrate the theoretical performance of perchloryl fluoride with a hydrocarbon fuel, a hydrazine fuel and a boron-containing fuel. Performance values, where available, are also included for these fuels with two other oxidizers, fuming nitric acid and liquid oxygen in order to indicate qualitatively the position of perchloryl fluoride in the performance spectrum.

III.   EXPERIMENTAL WORK AT AEROJET

A.   INTRODUCTION

Because no quantitative data were available on the ignition delay of perchloryl fluoride with various fuels, a program to investigate the ignition characteristics was initiated at the Aerojet-General Corporation under one phase of a contract from the Office of Naval Research. This investigation included cup tests, the determination of the ignition delay of unsym.-dimethylhydrazine with perchloryl fluoride and some preliminary ignition characteristics of monomethylhydrazine, and mixtures of 40 wt% unsym.-dimethylhydrazine and 60 wt% JP-4 with perchloryl fluoride.

B.   CUP TESTS

Two cup tests were made with the standard cup-test apparatus. For the first test, 6 ml of perchloryl fluoride, at -47°C, was added to 6 ml of unsym.-dimethylhydrazine. For the second test, 3 ml of perchloryl fluoride, at -47°C, was added to 3 ml of unsym.-dimethylhydrazine. After a barely perceptible delay, detonations occurred in both cases.

C.   IGNITION DELAY APPARATUS

The ignition delay tests were conducted with the Aerojet "elbow" motor. The apparatus consists of a 1-1/4-in. aluminum bulkhead elbow tapped for a replaceable impinging injector. A sonic nozzle is threaded into the chamber formed by the elbow, and a tap for measuring the pressure produced by combustion is provided. The pressures produced between the propellant valve and injector orifices are recorded on a multichannel oscillograph. The ignition delay is measured from the start of the rise of the injection pressure to the start of the rise of the chamber pressure. To avoid pressure surges from excessively long delays, and the subsequent propellant accumulation, a control unit is placed in the circuit between the firing switch and the propellant valve. This unit will close the propellant valve and terminate the test if a chamber

CONFIDENTIAL

pressure of 150 psi is not reached within a pre-set time after propellant injection. This time is normally set between 100 and 150 millisec. A second circuit limits the duration of combustion, generally 500 millisec, but adjustable to 4 sec. In addition, a safety diaphragm, designed to burst at 600 psig, was installed in the upper portion of the chamber to protect it against damage should extreme pressure surges occur.

D. IGNITION DELAY OF UNSYM.-DIMETHYLHYDRAZINE WITH PERCHLORYL FLUORIDE

1. A series of calibration runs were made, using red fuming nitric acid (15% NO_2) and unsym.-dimethylhydrazine, in order to obtain a basis of comparison for the proposed runs using perchloryl fluoride as the oxidizer. The average ignition delay of the unsym.-dimethylhydrazine and red fuming nitric acid system was 3 to 5 millisec.

2. Eight tests were carried out with the elbow motor using unsym.-dimethylhydrazine and perchloryl fluoride, utilizing a slight oxidizer lead. In all eight of the tests, the unsym.-dimethylhydrazine and perchloryl fluoride combination caused an explosion upon ignition, rupturing the safety diaphragm. The oscillograph tracings showed that the ignition delay ranged from 18 to 23 millisec after the unsym.-dimethylhydrazine entered the combustion chamber.

3. In an effort to avoid explosions and to obtain smooth combustion of the unsym.-dimethylhydrazine and perchloryl fluoride system, a splash plate was inserted in the combustion chamber of the elbow motor, just beyond the point where the fuel and oxidizer streams intersect. A series of seven test runs, made at several different mixture ratios, resulted in seven explosions when using the elbow motor equipped with the splash plate.

4. The oxidizer lead was eliminated, and the propellants were injected simultaneously, but this change still resulted in an explosive start. Use of a fuel lead also resulted in an explosion.

E. MONOMETHYLHYDRAZINE WITH PERCHLORYL FLUORIDE

Five test runs were made using monomethylhydrazine and perchloryl fluoride. Previously, the Naval Air Rocket Test Station reported that this system ignited and burned smoothly in a micro-motor. However, each of the test runs in the Aerojet-General elbow motor resulted in explosive ignition. No ignition-delay measurements were made during these runs.

F. 40% UNSYM.-DIMETHYLHYDRAZINE - 60% JP-4 WITH PERCHLORYL FLUORIDE

Four runs were made with the elbow motor, using a mixture of 40 wt% unsym.-dimethylhydrazine - 60 wt% JP-4 and perchloryl fluoride in order to determine whether this system would ignite smoothly. These runs were made using four different oxidizer-fuel mixture ratios that ranged from 2 to 4. During each run, an explosion accompanied the ignition. The ignition delay was not determined.

CONFIDENTIAL

G.   OBSERVATIONS ON THE CORROSIVE QUALITIES OF THE EXHAUST PRODUCTS
AND OF PERCHLORYL FLUORIDE

1.   Observations of the equipment used in these tests indicate
that severe corrosion resulted wherever the combustion products of the
fuel and perchloryl fluoride came into contact with the metal apparatus.
Both the stainless steel and aluminum were rapidly attacked, even though
the entire assembly was thoroughly washed with water and dried immediate-
ly following each test. Although some corrosion was to be expected be-
cause of the hydrochloric acid and hydrofluoric acid formed during the
combustion process, the actual corrosion was greater than was expected.

2.   When contained in stainless steel or aluminum, the per-
chloryl fluoride itself presented no particular corrosion problem. When
portions of the system were "bled" to the atmosphere, corrosion of alu-
minum occurred as a result of contact of the perchloryl fluoride with
moist air.

IV.   CONCLUSIONS

A.   The hard-starting characteristics of perchloryl fluoride with
hydrazine compounds under conditions of hypergolic ignition is definite-
ly a hindrance to the use of the material. The cause of this phenomenon
is believed to be the formation of an explosive intermediate compound.
The Pennsylvania Salt Manufacturing Company has reported that reaction
between perchloryl fluoride and certain nitrogen-containing compounds
such as ammonia and amines results in the formation of an explosive
solid. The compound $ClO_3NH.NH_4$ has been isolated and found to be ex-
plosive. The Pennsylvania Salt Manufacturing Co. is pursuing the study
of these reactions in the hope that some means of preventing the forma-
tion or destroying the intermediate as it is formed may be accomplished.
As demonstrated at both the Naval Air Rocket Test Station and General
Electric Co., with a slug start or preheating during the ignition may
be accomplished satisfactorily and the subsequent combustion is smooth.

B.   An additional property of perchloryl fluoride which requires
investigation, is that of heat transfer. For many applications the
oxidizer must be used to regeneratively cool the thrust chamber, and no
work has yet been reported on the feasibility of accomplishing this with
perchloryl fluoride.

C.   As stated by General Electric, the applications for perchloryl
fluoride would appear to be limited to those permitting a pressurized
system. Where the need for a storageable oxidizer of moderately high
performance arises, perchloryl fluoride can certainly be considered.

REFERENCES

1. Clark, John D., "Properties of Perchloryl Fluoride, A New Oxidizer for Rocket Fuels," NARTS 72, U. S. Naval Air Rocket Test Station, November 1955. (Confidential)

2. Forsten, I., "Experiments With the Oxidizer Perchloryl Fluoride in a Rocket Engine," NARTS 73, U. S. Naval Air Rocket Test Station, November 1955. (Confidential)

TABLE I

COMPARATIVE PERFORMANCE OF SOME SELECTED FUELS AND OXIDIZERS
$P_c = 300$ psia, shifting equilibrium

Propellants	Mixture Ratio (Optimum)	I_{sp} (lb-sec/lb)
UDMH - LOX	1.4	269
UDMH - ClO_3F	2.6	256
UDMH - RFNA (14% NO_2)	2.7	239
Ethyldecaborane - ClO_3F	4.4	245
Ethyldecaborane - RFNA (14% NO_2)	3.2	24?
JP-4 - LOX	2.3	262
JP-4 - ClO_3F *	3.?	249
JP-4 - RFNA	.?	230

* Calculated by General Electric Co.

GENERAL DISCUSSION

G. J. BRYAN (Naval Ordnance Laboratory): Provided a commercial method for the production of nitrogen trifluoride can be developed, do you know of any reason that perchloryl fluoride should be given further consideration?

DR. GANTZ: I have only recently considered nitrogen trifluoride. From this cursory examination, I would say that it would probably be competitive.

DR. NOEGGERATH: I have a question for either Ed or Bill. I have heard that the change in density of this material as a function of temperature is extremely wild and that its use as a storable oxidizer therefore is somewhat limited. As I understood it, the ullage required for the normal temperature range specification would be about 30%. I was wondering if my information is correct, and if it is, what are we going to do about it?

DR. GANTZ: It is true that the temperature variation of density is rather wide. I don't remember the exact figures on what the ullage would be. However, in a pressurized system you do minimize this density variation.

JOHN F. GALL (Pennsylvania Salt Manufacturing Company): The density of perchloryl fluoride does change rapidly with temperature above about room temperature. This is because we are not far from its critical temperature of 95°C. Every liquid, as it approaches its critical temperature, has to undergo a change of density so that its density can become equal to that of the vapor at the critical temperature. The density at 25°C is about 1.40 and the density at 50°C drops to 1.29. Conversely, we gain a great deal by lowering the temperature and with mild refrigeration we can go down to the boiling point where the density has risen to 1.69. If we wanted to, we could go all the way down to the melting point, which is -146°C, with a density of 2.0. A number of people have considered the advantages of using chilled perchloryl fluoride.

Another effect of being close to the critical temperature is that the compressibility of a liquid becomes great. Again, as a liquid reaches its critical temperature, its compressibility has to become equal to that of its vapor, which is very high. To calculate the allowable ullage for a given maximum temperature requirement, we can in this case permit the container to become liquid full. That is not ordinarily considered because, normally, when the container has become filled with liquid and the temperature rises any more, we expect an extreme rise in pressure. This does not occur when we are close to the critical temperature, which we are when we consider current upper temperature limits as high as 200°F. That's about all I can say on ullage.

On the explosion phenomena observed by Aerojet, we are not sure that it is caused by this intermediate compound. We are sure that it is not caused by any explosive character of perchloryl fluoride. The compound has a negative heat of formation, in the Lewis and Randolph sense, which means that heat is evolved when it is formed so that heat has to be absorbed by its decomposition. Furthermore, tests ranging from the ordinary drop tests and impact tests to the most severe that we can provide -- we have been using the perforation of the container by shaped charges which provide high impact and very high temperature at the same time -- show no explosive properties whatsoever.

Then one more statement, Bill Knight or Dr. Gantz, referred to the compound as being available in research quantities. It is available in more than that when needed. The process for making it is now well worked out, which is fairly rapid progress since the compound was just discovered in 1952. We can immediately supply smaller quantities for testing purposes, and we are ready to make any quantities that you need.

JOHANN G. TSCHINKEL (Army Ballistic Missile Agency): I'd like to know the critical pressure.

DR. GALL: 53 atmospheres.

PAPER

HIGH TEMPERATURE RESEARCH AT TEMPLE

by A. V. Grosse, C. S. Stokes, W. L. Doyle
(Presented by Dr. Grosse)
The Research Institute of Temple University

(See pages 188 to 192, this volume)

PREPARED DISCUSSION

None

GENERAL DISCUSSION

JOHN HAPPEL (New York University): In connection with Dr. Grosse's remarks on acetylene compounds, I thought some work we did four years ago at NYU under the sponsorship of ONR might be of interest. We made about 40 acetylenic compounds to test in bipropellant rocket systems. Among them was monoacetylendinitrile. It was made by a complicated synthesis and cost us about $200 per pound. What is interesting, though, is that it showed a very high specific impulse, higher than any other acetylenic compound; 244 sec with RFNA at 300 psia chamber pressure and frozen equilibrium. This compared with a value of 241 sec for acetylene, the compound with the next highest specific impulse.

We thought, in view of the relatively high melting point of this material, 69°F, mixing it with mononitrile might result in a more useful fuel, if a synthesis method could be found that would get the price down, of course.

ERNST A. STEINHOFF (Holloman Air Force Base): I'd like to ask Dr. Grosse whether anything is known about the boiling point of O_3F_2 and, secondly, whether he thinks that there are compounds of higher complexity beyond O_3F_2 possible?

DR. GROSSE: We do not know exactly the boiling point of O_3F_2 except that it begins to decompose at -150°C into O_2F_2 and oxygen; that is, at this stage of the art, because the compounds are obviously not as pure as they should be.

MR. STEINHOFF: Do you think that there are possibly compounds of higher complexity -- beyond O_3F_2?

DR. GROSSE: Yes, the Japanese report contains information of that nature.

LOREN BOLLINGER (Ohio State University): On the hydrogen fluorine premixed flames was there any attempt made to purify the fluorine; from what company did you obtain the fluorine; and was there any investigation made of the material used in your burner tubes and connecting lines?

DR. GROSSE: I would not like to answer that in just a few minutes, Dr. Bollinger, as I do have slides and other material and would be glad to discuss them with you, because I think time is short.

27 MARCH 1957
AFTERNOON SESSION

CHAIRMAN: DR. D. L. ARMSTRONG

DR. ARMSTRONG: One of the areas that certainly deserves as much attention as can be given to it is that of the toxic hazards of propellants that we are working with at this time. All too often this has become a secondary consideration and the result has been that many people have been injured through exposure to toxic fumes, and in some cases received permanent damage to their internal organs, while a little attention to this detail might have resulted in taking more adequate precautions.

PAPER

TOXIC HAZARDS OF LIQUID PROPELLANTS

by Keith H. Jacobson
Army Chemical Center

(See pages 78 to 84, Volume 1, PFL 212/13)

PREPARED DISCUSSION

None

GENERAL DISCUSSION

DR. ARMSTRONG: Would you care to recommend a frequency for clinical examinations for persons exposed to normal rocket testing procedures?

DR. JACOBSON: I don't feel able to answer that question. There are so many variables involved; the particular fuels that you are dealing with, the adequacy of the safety precautions that you have, the experience you have had in the past, the personal preferences (which are, of course, based on personal experience) of the physician in charge, etc.

WILLIAM G. STRUNK (Westvaco-Chlor Alkali Division, Food Machinery & Chemical Corporation): It occurred to me that it might be of interest to bring out manufacturing experience with some of these chemicals. Westvaco has now been manufacturing Dimazine-brand unsym-dimethylhydrazine for several years. We have had a very excellent safety record with the material with no cases of acute poisoning and no evidence of chronic poisoning.

Our medical surveillance program includes a complete physical examination before a man starts to work on this operation and those who show evidences of anemia or liver disease are not put to work. At intervals of six weeks hemoglobin and white blood cell count are made.

The basic safety precautions we give our men include wearing a respirator with an ammonia canister if they can smell the material when they are working with it. The other one is the use of splash-proof goggles and vinyl-coated gloves.

In case of danger of gross splashage, suitable splash-proof garments should be worn. They can then be removed and laundered if and when a splash does occur.

MR. ROSCOE LIBBY (Air Materiel Command): I shuddered a little bit this morning when the good doctor said "You just dump it down the drain," because I am the man on the other end of the drain who gets it. We have the disposal problems for this material when you boys are done playing with it.

I can't give you the exact figures; however, I will give you a figure that is closer to the actual figure than you would think. There will be approximately 100,000 gallons of Type IIIA red fuming acid to dispose of every week. This RFNA is cycled in the missiles periodically and when it goes out of specification it must be disposed of or destroyed. That is a lot of material and it can't be disposed of by any common ordinary method. For example, this RFNA has a specific gravity of approximately 1.5 and weighs 12 to 12-1/2 pounds per gallon. Around seven or eight gallons of this material after it is neutralized is all that a million gallons of water can absorb and still stay within

most of the State laws for nitrate in potable water -- which are around ten parts per million maximum. When we have a large amount of RFNA coming in every day -- say 100,000 gallons a week -- that is a lot of standard sized tank cars of acid. It would take a lot of water to dilute that much nitric acid. Before this material can be neutralized or diluted the nitrogen dioxide must be taken care of, usually by some oxidation process. We have tried burning this NO_2. The last documented cost figures that I have on an experimental method of burning these NO_2 fumes are between $1.00 and $1.50 for a gallon of acid neutralized. (This includes the cost of the neutralizing chemicals). When a large amount of RFNA is to be disposed of every week, even $1.00 a gallon runs into a lot of money.

We can oxidize this NO_2 into nitric acid, using for instance, waste hydrogen peroxide. We could use some dichromate salt such as sodium or potassium dichromate. After the NO_2 has been converted to nitric acid the neutralization problem still remains as does the problem of what to do with the nitrates and fluorides. We can't pond or lagoon this waste due to the hazard to underground water supplies, and we can't dispose of it in streams. There is a possibility of desert disposal or in pumping the neutralized, clarified waste to underground formations through disposal wells. I don't have any quick solution for this problem. I may be a little out of order in bringing up the Industrial Hygiene hazard connected with the disposal of rocket propellants and oxidizers, but the men at waste disposal plants will get this material to dispose of -- it will come in unidentified -- the industrial waste plant workers will have to find out what the material is, and then will have to decide what method of disposal to use. These materials are difficult to dispose of even when they are identified.

I think that we have worked out some solutions to this industrial waste disposal problem, but I think that some of it could be reprocessed or remanufactured. No manufacturer of inhibited red fuming nitric acid that we have approached has shown any inclination to take any of it back, especially when it has the hydrofluoric acid in it. We have offered to take the hydrofluoric acid out or to arrest its aggressive properties, but we still haven't had any offers -- not any reasonable offers. We can buy the new acid cheaper.

DR. JACOBSON: I have no information on the best methods of disposal. I have the impression that somebody is working on that, but I am not sure.

One item I might mention is that as far as we can find out, the addition of small amounts of hydrogen fluoride to red fuming nitric acid does not significantly alter its toxicity. What effect this has on the disposal problem, I do not know.

VOICE: I have been led to believe that the halogen fluorides are of the same order of toxicity as fluorine or HF; namely, a

tenth of a part per million, as indicated in your paper. This, of course, does not include the perchloryl fluoride. Would you care to comment on this?

DR. JACOBSON: The only one that I can comment on is fluorine oxide. I did not include that because of a number of reasons, one of which is the lack of evidence available. There is evidence that fluorine oxide is appreciably more toxic than fluorine. There has been some suggestion that this does not hold true in man; if so, this is one of those rare cases where animals and men don't react alike. My own viewpoint is that we must assume fluorine oxide to be appreciably more toxic than fluorine.

DR. ARMSTRONG: I think the point that the disposal problem is a serious one is well taken and deserves serious attention of those concerned with that type of operation.

<u>PAPER</u>

<u>HEAT TRANSFER PROPERTIES OF ANHYDROUS AMMONIA</u>

by T. F. Reinhardt, R. L. Potter, F. M. Moore
(Presented by Dr. Reinhardt)
Bell Aircraft Corporation

(See pages 85 to 97, Volume 1, PIL 212/13)

<u>PREPARED DISCUSSION</u>

by Robert W. Ellison
Reaction Motors, Inc.

(See following pages, 30 to 32)

<u>GENERAL DISCUSSION</u>

None

R. W. Ellison
Reaction Motors, Inc.
Denville, New Jersey

Prepared Discussion on Paper by T. H. Reinhardt, R. L. Potter,
and F. M. Moore

HEAT TRANSFER PROPERTIES OF ANHYDROUS AMMONIA

The paper, "Heat Transfer Properties of Anhydrous
Ammonia", by T. H. Reinhardt, R. L. Potter and F. M. Moore
modestly minimizes the difficult nature of heat transfer determina-
tions. The background revealed by References 1, 2 and 3 clearly
indicates the accomplishment, and accordingly, L. E. Dean, E.
Ashley and the authors are commended for their solution of a con-
siderable problem.

The discussion is presented in a clear and forthright man-
ner appropriate to its purpose, and the authors' wisely directed at-
tention to the references for derivation of the equation used to eval-
uate the liquid side wall temperature. The data are presented
graphically and form a visible picture of the properties of ammonia
for the range of parameters reported. The bulk of the properties
data appears in Figures 3, 6 and 7. Correlation of measured data
is shown for two relations in Figures 4 and 7. The significance of a
composite plot of nucleate boiling data, Figure 5, is somewhat mys-
tifying.

The authors have included an exacting description of the
test section used both here and in the first group of references listed.
Critical dimensions are reported in at least three significant digits
whose use implies the great care exercised to control these signif-
icant parameters. In general the experiments appear to have been
executed with great care, and, overall, the results are admirably
reported.

Correlation of data is the subject for approximately one-
third of the text, and the attempts at correlation are wisely divorced

for the non-boiling, nucleate boiling and burnout regimes. The n-boiling data are visibly compared with the Dittus-Boelter Equation in Figure 4, and the overall appearance of the individual dots indicates that there are roughly the same number of data points above the theoretical curve as there are below. The evident scatter includes an appreciable number of data points which are rather distant from the curve. The extent and degree of scatter are such that the Dittus-Boelter equation cannot be confirmed for the non-boiling regime with absolute certainty.

Before absolute confirmation is warranted, it appears necessary to reduce the incidence of data-points which fall far distant from the curve of the Dittus-boelter equation. Possibly an improvement in the thermometry would contribute to less scatter; it appears more likely, however, that a part of the evident scatter may have resulted from the entrance of linear velocity into the equation under the comparatively high exponent of 0.8. Lacking complete knowledge of the velocity distribution across an annulus subject to heat transfer, the exact meaning and value of V, the symbol for "effective linear velocity" of the fluid, are not completely established.

The second discrete discussion of the correlation deals with nucleate boiling. No correlation was claimed or possible in the case of ammonia since the probable thermometric errors were larger than the values of ΔT_{sat} used in correlation. A detailed analysis of the evaluation of saturation temperatures and the use of resistance thermometers is indicated for the successful correlation on nucleate boiling data for ammonia. Nucleate boiling experiments over wide ranges of pressure and bulk temperature would also be interesting. These parameters might affect the location or slope of the nucleate boiling line given a sufficient range. Determinations at higher pressures would be of particular interest in such investigation.

Burnout data and its correlation are discussed in a third section referring to two equations. The one used by Ashley for WFNA data is limited in range; the other uses the value of burnout flux obtained by JPL in hot-wire tests. The correlation as shown in Figure 7 is evident, but the majority of experimental data points is concentrated at a single value of ΔT_{sub}, approximately 120°F. The paucity of points at other values precludes the conclusion that equation 6 is confirmed for burnout in the case of ammonia. The close agreement of the points marked is, however, indicative of confirmation over the range tested. Visually, Figure 7 indicates that burnout is but slightly affected by the fluid velocity.

One overriding question arises, howe·er, in connection with the values of pressure; it is not ment··d whether the values listed are the true static pressure at the mid-point of the test section or are simply the gauge readings taken either upstream or downstream. At low velocities the differences in values for the various concepts are not large. At the highest velocity mentioned, 125 feet per second, the kinetic pressure loss is roughly 40-60 psi depending on the conditions of the fluid.

A statement precluding possible ambiguity with respect to pressure would also have been useful with respect to the saturation temperature, T_{sat}, and the scale parameters derived from it, ΔT_{sub} and $T_w - T_{sat}$. At low velocities the kinetic pressure loss has but little effect; at 125 feet per second velocity, the maximum error in ΔT_{sat} resulting from the use of uncorrected gauge readings would not exceed 10 to $20^\circ F$. At low values of $T_w - T_{sat}$ and of ΔT_{sub}, the distinction between true static pressure at the test section and readings taken elsewhere (at low velocity points) is critical. If the references obviate the question of which concept was used, it has escaped notice, and a statement within the paper under discussion seems in order. (This same ambiguity in concepts of pressure has been widespread in the heat transfer reports of most groups working in this field.) The authors mention that data from JPL "show a lower dependence of $(q/A)_{burnout}$ on ΔT_{sub} than is shown by our (?··?·) ··sults." It appears possible that different concepts of pressure may have contributed to the difference in results.

The paper also permits a small question concerning the possible solution of gas used to pressurize the ··· ··· Ordinarily the effect would not warrant mention, but ·· a·· ·····able solubility of nitrogen (if nitrogen was used) raises some concern in the case of ammonia.

In this work, it has been chosen to use a volumetric flow-meter and to report values of linear velocity, V. The alternative use of tank-supporting load cells or of one of the true mass flowmeters would appear more direct and less limited in accuracy, for values of linear velocity were evidently computed by a form of Bernoulli's T'···)rem which inherently contains mass as the conservative quantity. While these "volume" and "velocity" practices are not uncommon, it is submitted that mass velocity, G, is more meaningful and more reproducible in ducted flow than is the concept of an average fluid velocity.

PAPER

PETROLEUM DERIVABLE NITROGEN COMPOUNDS AS LIQUID ROCKET FUELS

by J. E. Mahan. H. M. Fox, H. W. Bost, O. E. Larsen, R. C. Doss
(Presented by Dr. Doss)
Phillips Petroleum Company

(See pages 98 to 114, Volume 1, PFL 212/13)

PREPARED DISCUSSION

J. D. Clark
US Naval Air Rocket Test Station

(See following pages, 34 to 36)

GENERAL DISCUSSION

None

Discussion Prepared by
John D. Clark
U. S. Naval Air Rocket Test Station
Lake Denmark, Dover, New Jersey

on Mahan, Fox, Bott, Larsen and Doss's Paper
PETROLEUM DERIVABLE COMPOUNDS AS LIQUID ROCKET FUELS

In the first part of this paper the authors have described
a rather interesting series of compounds which appear to be roughly
comparable to UDMH as rocket fuels.

The question at once arises as to whether or not they are
sufficiently superior to present fuels to warrant serious consideration.
If we compare a typical example: N, N, N^1, N^1 tetramethyl butane
1, 3 diamine, with UDMH, we find something like this:

Specific impulse:	2.9% worse than UDMH
Density impulse:	1.9% better than UDMH
Hypergolicity:	Good, but inferior to UDMH
Viscosity:	Good, but inferior to UDMH
Boiling point and vapor pressure:	Better than UDMH
Freezing point:	Better than UDMH, but below -72°F it makes little difference
Density:	Little to choose
Thermal stability:	Probably better than UDMH
Compatibility:	Little to choose
Additive to JP:	Inferior to UDMH

In short, there is so little difference between the two compounds, that
any decision between them would probably be made on logistic grounds --
availability and price. The authors, unfortunately, have given no
information as to how the logistics of these compounds compare with
UDMH.

The second part of the paper deals with monopropellants made
by dissolving the nitrate salts of these tertiary diamines in nitric
acid -- producing solutions comparable to the monopropellant Isolde
developed at NARTS. Isolde, as you probably know, consists of the
nitrate of diisopropyl amine dissolved in nitric acid.

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In order to shorten the discussion by an order of magnitude I am going to take the liberty of christening "N , N , N^1, N^1-tetramethyl-butane-1, 3 diamine dinitrate dissolved in anhydrous nitric acid," "Beatrice" for short, and the analogous propane propellant can be called "Portia."

The work with Beatrice and Portia confirms several of the observations we have made at NARTS on Isolde and similar compounds.

First -- they have a poor thermal stability. At 60°C - 140°F - Portia built up enough pressure in 145 hours to blow a 100# burst disc, and Beatrice only took 57 hours. Our Minnie -- the tri-methyl amine propellant -- would take about 100 hours to do the same. (This is an estimated value--the burst times at several higher temperatures being extrapolated to 60° by the Arrhenius equation, which describes the phenomenon quite accurately.) We have found that such propellants made from tertiary amines are in general thermally unstable. If a sample of the completed propellant is placed on the steam bath, it invariably ignites before all of the acid has been evaporated. If Isolde (made from a secondary amine) is treated the same way, the acid evaporates off, and the salt is recovered almost quantitatively, with only a slight discoloration. The extrapolated burst time for Isolde at 60° would be something like 3500 hours.

The viscosity data, too, confirms ours. Early in the game we found that propellants made from diamines had a high viscosity and a high temperature coefficient of viscosity compared with those made from mono-amines. The viscosities of Portia, Beatrice, and Isolde, at 75°F, are 6.1, 4.7, and 1.9 centistokes respectively, and at -40° they are 108, 62, and 11.8.

The card-gap values for Portia and Beatrice (12 cards) are low (Isolde under the same conditions gives 20 cards) and are close to the 14 card value for Minnie. An extensive series of card-gap tests at NARTS has resulted in a remarkable correlation between structure and sensitivity for amine-nitrate monopropellants -- and by that correlation it would appear that when a carbon chain is tied down at both ends by an amine group, the only carbons in the chain that contribute to the sensitivity are those adjacent to the nitrogens.

There are two more observations that I have to make. The first is that we have done a little work ourselves on amine perchlorate monopropellants and have found that they have an extremely high shock sensitivity, and that when they go the results are devastating. So, if you wish to work with such things -- don't!

The second is on the use of HF as a corrosion inhibitor in amine nitrate monopropellants. We have found that it is unnecessary with aluminum, having no particular effect on the already very low corrosion rate. With stainless steel (347) it makes the low corrosion rate much worse.

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The opinions expressed in this discussion are those of the author, and are in no wise to be construed as representing those of the Naval Air Rocket Test Station, of the Bureau of Aeronautics, the U. S. Navy, or the Department of Defense.

DR. ARMSTRONG: I think that anyone who has been in the rocket business very long realizes that we are rapidly approaching the limit of performance obtainable with ordinary chemical propellants. I believe that Zowicki first proposed the use of metastable states for propulsive means. This idea lay dormant for several years and was finally taken up by the Directorate of Advanced Studies of the Office of Scientific Research. That was about three years ago, I believe. Since then interest has increased exponentially so that today there are many programs all directed toward the utilization of free radicals as a means of propulsion. Lieutenant Colonel Atkinson of the Office of Scientific Research will tell us about the free radical program.

PAPER

SURVEY OF RESEARCH ON FREE RADICALS AS PROPELLANTS

by Paul G. Atkinson
Air Force Office of Scientific Research

(See pages 1-17, Volume 1, PFL 212/13)

DR. ARMSTRONG: Probably the largest single program in the country at this time on the subject of free radicals is that of the Bureau of Standards, and prominent in the organization and initiation of that program is Dr. Broida, who will offer comments on Colonel Atkinson's paper.

PREPARED DISCUSSION

by H. P. Broida
National Bureau of Standards

(See following page)

GENERAL DISCUSSION

None

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Discussion Prepared by
H. P. Broida
National Bureau of Standards
Washington, D.C.

on P. G. Atkinson Paper
SURVEY OF RESEARCH ON FREE RADICALS AS PROPELLANTS

Colonel Atkinson's presentation of the research on free radicals as propellants has covered the major points of potential uses and advantages of free radical fuels. Quite rightly he has not concentrated on pointing out the difficulties of the use of such materials. At this stage of scientific progress it is not a question of how to use such fuels. The question is – can enough energy be stored in stabilized free radicals for potential use as a fuel?

Recent laboratory results show that even highly reactive free radicals can be stored for long times in solids at low temperature. In addition, it has been found that concentrations above 1% can be stabilized under certain conditions. In view of these results and the relatively small concentrations needed for good specific impulse performance (see page 3 of Atkinson's report), it is essential to determine the upper physical limit on the concentrations so that an answer can be given to the question on whether sufficient energy for use as a propellant can be stored in free radicals. Until this question is answered in the affirmative, it is premature to dwell too deeply on the question of how to use such a fuel.

I should like to stress two points already mentioned by Colonel Atkinson. First, in his definition of the term "free radical", he properly omits other species in which energy is available. Unfortunately there is some confusion caused by those who lump together other energetic species such as ions or electronically excited molecules. While such species might be useful as propellants, their properties are much different from those of free radicals. The second point that bears repetition is the one that only a few radicals – simple and of low molecular weight – have any potential use as fuels. The specific impulse obtainable from most free radical reactions is too small to be of value as a fuel.

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PAPER

THEORETICAL AND EXPERIMENTAL EVALUATION OF SEVERAL AMINE FUELS, WITH FUMING NITRIC ACID

by J. S. Gordon
Reaction Motors, Inc.

(See pages 115 to 135, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by H. W. Fox
Phillips Petroleum Company

(See following pages, 40 to 43)

GENERAL DISCUSSION

None

Discussion Prepared By
H. M. Fox
Phillips Petroleum Company
Bartlesville, Oklahoma

on J. S. Gordon Paper
THEORETICAL AND EXPERIMENTAL EVALUATION OF
SEVERAL AMINE FUELS, WITH FUMING NITRIC ACID

Because we have pioneered the tertiary diamines as possible
nitric acid rocket fuels, it was gratifying that these fuels, for the
most part, performed satisfactorily in the WADC engine tests. These
data obtained on several compounds over a wide range of mixture ratios
are the most extensive which have been reported. In general, the data
confirm the theoretical possibilities of these fuels and the indi-
cations, obtained by the Naval Ordnance Test Station in the LAR and
simulated-LAR engines, that the tertiary diamines compare favorably
with hydrazine and UDMH.

We have a few comments about Table II of the WADC paper which
summarizes some of the important properties of the tertiary diamines.
The question might be asked: Why have the unsaturated species been
considered by Phillips to such an extent in view of their thermal in-
stability characteristics? The unsaturated species have advantages in
yields and in manufacturing costs; we are not convinced that their
thermal instability is as serious as indicated by Gordon. We believe
that the thermal instability is caused by minor amounts of water which
were not removed in the manufacture or were added in storage, and it
seems reasonable that something can be done to eliminate or to reduce
significantly this effect of moisture. We have observed that some of
the unsaturated species compare favorably with the saturated species
in storage behavior when a desiccant is added to the stored sample.
For example, N,N,N',N'-tetramethylbutene-1,3-diamine appeared unaffected
by heating for one hour at 500 F when metallic sodium was present in
the sample. While particulate matter would not be desirable in a
rocket fuel, we believe that a satisfactory solution could be evolved
with minor effort.

This adverse effect of moisture might account for the
questionable heat of combustion for N,N,N',N'-tetramethylpropene-1,3-
diamine given in Table II of the paper. We have obtained erratic
results on this compound. On the basis of several careful determinations

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we have settled on a value of 17,017 Btu/lb which is more reasonable than the one given. We believe it to be a considerably better value.

We do not feel that the deposit problem with N,N,N',N'-tetra-methylethane-1,2-diamine in cooled nozzles is serious. Analysis of these deposits showed that they were the nitric acid salt of this tertiary diamine which from its thermal stability behavior could only form on cooled surfaces during shut down. The salt formed under such conditions could be tolerated in most applications. In cases in which it could not be tolerated, formation of the salt could be prevented by simple means.

One of the most interesting aspects of the WADC data was the rather large differences in combustion efficiency observed between the various compounds many of which are similar in physical and thermo-dynamic properties. The following summarizes the combustion efficiency results:

Fuel	η_c - Combustion Efficiency, %	
	200-lb, 110-L* Uncooled Engine	100-lb, 144-L* Engine
Tertiary Diamines	99-100 (2 fuels)	98-100 (6 fuels)
UDMH	98	-
MMH	-	98
MMH/UDMH Eutectic	-	96
DETA/UDMH 50/50	96	-
N,N-Dimethylamino-3-propylamine	93	-
DETA	90	-
Triethylamine	-	91

Combustion efficiency is defined for this consideration as actual c^* divided by theoretical c^*. Theoretical data used were frozen-equili-brium data in which the following products of combustion were assumed: CO_2, CO, H_2O, N_2, H_2, O_2, O, H, OH, and NO. Actual and theoretical values of c^* used in the analysis were peak values regardless of mixture ratio. A plot of combustion efficiency as a function of mixture ratio for the fuels showed the same relationship between fuels as the preceding tabulation.

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The data for neat fuels are divided into two distinct ranges of combustion efficiency: (1) 98-100 per cent range, and (2) 90-91 per cent range. These data are limited but it seems more than accidental that all of the fuels giving good combustion efficiencies are highly reactive fuels with nitric acids, as measured by ignition delays, compared to the poor fuels which have very long ignition delays or are not hypergolic. DETA which is not hypergolic gave the lowest efficiency and exerted an almost additive effect in an adverse direction on the UDMH mixture. It is difficult to explain the difference in the performance of the diamines and triethylamine on the basis of better engine optimization for the diamines because physically and thermodynamically they are essentially the same. These data emphasize the need to consider kinetic properties in the selection of nitric acid rocket fuels. They cast doubt on the assertion so often heard, that in selection of liquid rocket fuels we need consider only theoretical performance, physical properties, and cost and that kinetic deficiencies can be easily ironed out by engine design and development. We believe these data support the contention that better screening of liquid rocket fuels should be done in actual engine firings; as a result, engines could be developed and made to operate at less cost.

A parameter of substantial significance in some applications such as rocket projectiles, particularly air-to-air missiles, is volume impulse. We were interested to see how the fuels tested by WADC compared on this basis. Figure 1 is a plot of volume impulse versus specific impulse obtained on fuels tested in the 200-lb engine. Units of volume impulse are impulse per cubic foot of propellants. Differences obtained are because of differences in specific impulse and mixture ratio. For N,N,N',N'-tetramethylethane 1,2-diamine and UDMH which peak at approximately the same specific impulse, the former was almost 8 per cent superior in volume impulse. One of the reasons for considering the DETA/UDMH mixture was, of course, to improve volume performance over that obtainable with UDMH. Certain advantages of the mixture in this respect are evident from these data. However, at the peaks the superiority in volume performance of the mixture was slight compared to the loss in specific impulse.

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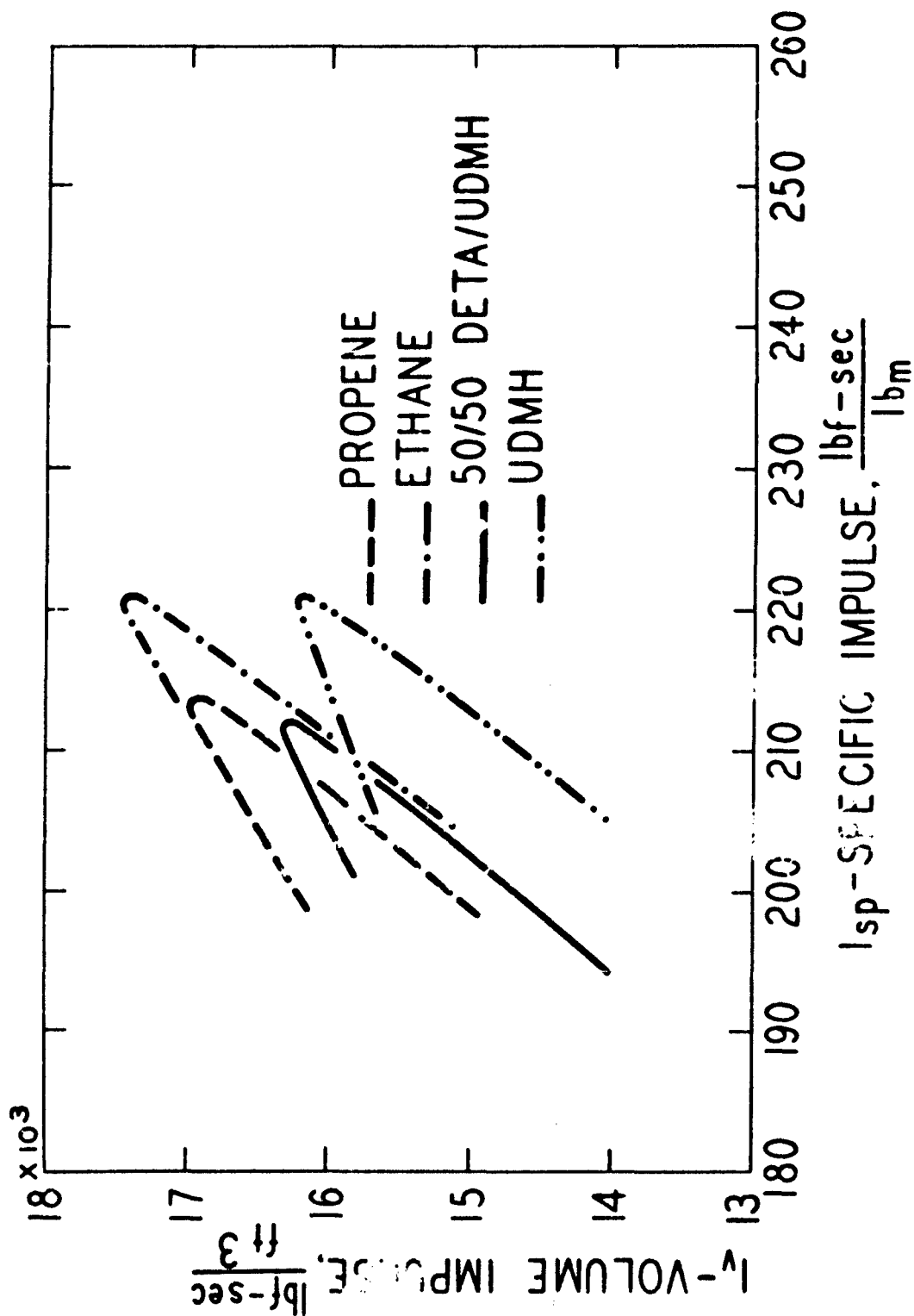
FIGURE 1

SPECIFIC IMPULSE VS VOLUME IMPULSE

PAPER

DESENSITIZATION OF LIQUID MONOPROPELLANTS TO
ADIABATIC AIR COMPRESSION IMPACT BY THE ADDITION OF ETHYLENE OXIDE

by C. W. Tait and W. A. Cuddy
(Presented by Dr. Tait)
Wyandotte Chemicals Corporation

(See pages 136 to 149, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by E. C. Noonan
US Naval Ordnance Laboratory

GENERAL DISCUSSION

None

Discussion Prepared by
E. C. Noonan
U. S. Naval Ordnance Laboratory

on C. W. Tait and W. A. Cuddy Paper
DESENSITIZATION OF LIQUID MONOPROPELLANTS
TO ADIABATIC AIR COMPRESSION IMPACT

The authors of this paper should be congratulated on this interesting study of the impact sensitivity test. They illustrate very vividly that, contrary to a widespread notion, it is not the total potential energy available from the weight that is important in an impact sensitivity experiment but rather the elastic properties of the parts which are hit. These constitute a bottleneck through which the available energy must be transferred. Only a small part of the total energy available can participate in initiation of the explosive. They indicate the sensitivity of the final temperature reached by adiabatic compression on the specific heat ratio, γ, for the working gas. They point out the problem of propagation of an explosion from a hot spot and demonstrate the effect of heat conduction in an ingenious manner. Finally, they have made a practical suggestion on how to desensitize a particular explosive.

Tait and Cuddy found a linear dependence of maximum pressure in the liquid on the height of drop of the weight. They mention that the pressure should be a function of the square root of the height. It is interesting to see how this comes about and what general conclusions we can draw about the behavior of impact testers.

When a bar moving with a velocity u hits another bar at rest the maximum compressive stress at the plane interface of contact normal to the common axis of the bars is

$$P = \rho c \, u \qquad\qquad (I)$$

where ρ and c are the density and speed of sound respectively in the bar at rest (1). The instantaneous velocity of a mass initially at rest which has fallen from a height h is

$$u = \sqrt{2 \, g \, h} \qquad\qquad (II)$$

Finally the speed of sound c, may be expressed as:

$$c = \sqrt{E/g\,\rho} \qquad\qquad (III)$$

where E is Young's modulus in engineering units (1). We may combine equations (I), (II), and (III) to yield:

$$P = \sqrt{2\,E\,\rho\,h} \qquad\qquad (IV)$$

Substituting the proper constants for steel and the proper units for h in inches one finds that:

$$P' = 4080\sqrt{h} \quad \text{where P is in psi, h in inches}$$

$$P = 278\sqrt{h} \quad \text{where P is in atm, h in inches}$$

If one computes the pressures expected from this formula and compares them with those measured by Tait and Cuddy it turns out that they are of the same order of magnitude but from 45% to 6% too high. The actual situation in the impact tester is of course very complex, since there will be reflections at various points in the apparatus. As a matter of fact if the acoustic impedance of the parts were properly matched the full pressure should be reached on the first impulse, and the pressure records of Tait and Cuddy indicate that this is certainly not true.

Using the approximation for pressure given by equation (IV) and substituting in the pressure temperature relation for adiabatic compression the following equation may be developed.

$$T_2 = T_1\,(k/P_1)^{\frac{\gamma-1}{\gamma}}\,(h)^{\frac{\gamma-1}{2\gamma}} \qquad\qquad (V)$$

where k is the proportionality constant (278) of equation (IV) and γ is the ratio of specific heats. By differentiating T_2 with respect to one variable at a time, holding the others constant, one obtains four equations for dT_2. Combining these one finds the three equations for the relationship of the variables which produce the same change, dT_2 in T_2.

$$\frac{dh}{h} = \left(\frac{2\gamma}{\gamma-1}\right)\frac{dT_1}{T_1} \qquad\qquad (VI)$$

$$\frac{dh}{h} = \frac{-2dP_1}{P_1} \qquad\qquad (VII)$$

$$\frac{dh}{h} = \frac{4.606}{(\gamma^2-\gamma)}\,(\log k/P_1 + 1/2\,\log h)\,d\gamma \qquad (VIII)$$

To illustrate the magnitude of the effects one may investigate the behavior under the conditions that dh = 1 inch, h = 10 inches, $T_1 = 300°K$,

$P_1 = 1$ atm, $k = 278$ atm. Then to make an error of 10% in h significant, T_1 must be controlled to $\pm 4.3°C$, P_1 to ± 0.05 atm and γ to ± 0.0041 units. The sensitivity of the test to variation in γ is very apparent. In fact, under the above conditions, it can be shown that merely saturating dry air with water vapor at 300°K makes enough difference in γ to increase h from 10 inches to 11.3 inches. Even if the pressure developed is a linear function of drop height, as Tait and Cuddy found, the results are not much different. Using the equation

$$T_2 = T_1 (123\ h/P_1)^{\frac{\gamma-1}{\gamma}}$$

one finds that

$$\frac{dh}{h} = \left(\frac{2.303}{\gamma^2 - \gamma}\right)\left(\log \frac{123h}{P_1}\right) d\gamma$$

Under the same conditions used above, an error of ± 1 inch in h at 10 inches can arise from an error of $\pm .0079$ units in γ.

The dependence of the temperature, T_2, on drop height is also of interest. Taking P_1 as unity, $k = 278$, we find for various values of γ (equation V):

$$\gamma = 1.27 \qquad T_2 = 3.32\ T_1\ h^{0.106}$$

$$\gamma = 1.40 \qquad T_2 = 5\ T_1\ h^{0.143} = 5\ T_1\ h^{1/7}$$

$$\gamma = 1.66 \qquad T_2 = 9.4\ T_1\ h^{0.113}$$

Thus at $\gamma = 1.40$, the upper temperature reached depends on the 1/7 power of h! Of course T_2 must appear in the equation for reaction rate in some exponential form, as $k = Ae^{-E/RT}$ for first order kinetics.

Murgai (2) has published a theory of impact machines using the Hertz theory of impact. The particular model he used involved a steel ball impacting solid explosive on a flat anvil. An elaborate treatment involving the masses of the weight and anvil; Poisson's ratio, coefficient of restitution, shear modulus of steel, etc. leading to a calculation of radial pressure distribution is given. The net results of Murgai's treatment and that of the author may be compared for a given set of conditions when $P = 1$ atm and the various parameters of Murgai's equation remain constant; i.e., the same machine is used for the experiments.

Murgai	Noonan
$T_2 = k_1\ T_1\ h^{3/5\ (\gamma-1)/\gamma}$	$T = k\ T_1\ h^{3/6[(\gamma-1)/\gamma]}$

47

Values of T_2 obtained are very nearly the same when numerical values are substituted.

The above remarks are made mainly to disillusion those who think of an impact machine as a precision instrument and to indicate the outrageous degree of control necessary in order to expect reproducible results.

The equations of motion of a bubble under compression by a liquid medium and the nature of its behavior when chemical reaction occurs in the bubble are very interesting and complex. Enig, at NOL, has attacked this problem from a theoretical viewpoint with the aid of numerical integration techniques using high speed computers. So far he has shown that nitroglycerine detonates under certain, rather mild conditions, but at this point not enough data have been gathered to define the bubble size or compression ratio below which burning or detonation will not occur. We hope that these computations will be completed in the near future.

If a bubble of gas immersed in liquid is suddenly compressed it overshoots the equilibrium position, and, if it is stable, will oscillate with damped harmonic motion about the equilibrium size. In practice, however, it is easy to reach unstable conditions at high rates of loading. In this case the bubble breaks up on expansion. Essentially what happens is this: the inner surface of the bubble reaches fantastic accelerations during compression. If the mass of the particles in the surface is multiplied oy this acceleration one gets an inwardly directed force which is counterbalanced by the opposing force due to pressure of the gas and surface tension of the liquid. (Cohesive forces of the liquid may be neglected.) If Bernoullis' equations of motion for the liquid around the bubble are obeyed then its behavior would be stable. At radial velocities approaching the speed of sound instability may appear. The result is that at the time the bubble should start expansion, jets of liquid are sprayed in toward the center and the bubble breaks up into little bubbles. Some high speed photographs by J. B. Levy and A. Amster of NOL illustrate these effects.

If droplets are sprayed into the hot gas, or if new small bubbles are formed, the gas may be cooled before propagation of combustion can occur. Tait and Cuddy illustrate the effect of heat conduction by use of insulation. Consider this effect greatly multiplied by spray cooling and it is easy to see why propagation may not occur in many cases.

Thus, while it is true that high temperatures should be reached during truly adiabatic compression there are three good reasons why propagation of combustion may not occur.

a. The compression phase is not truly adiabatic; heat is lost to a relatively large mass of liquid over a relatively long time.

b. Instability of the bubble may result in sprays or jets which cool the gas rapidly.

c. The induction time for the chemical reaction is longer than the time available before the gas has cooled or impulsive loading has been relieved.

Once combustion has started within a bubble, it appears from Enig's analysis that intense shock waves can build up very rapidly. The fact that all the heat is being produced in a small, totally enclosed volume coupled with the inertia of the liquid makes this possible. If the liquid can support detonation this process will start soon after combustion begins. In the case of nitroglycerine, if 3% of the vapor originally assumed present reacts chemically, the rate of heating by reaction exceeds the rate of cooling due to expansion and detonation occurs almost immediately. If less than 3% reacts the cooling due to expansion quenches the reaction.

In summary, it may be said that Dr. Tait and Mr. Cuddy have made a distinct contribution to our understanding of impact tests and their interpretation. It is obvious that a great deal more needs to be done before a clear understanding of all the factors entering into the sensitivity of liquid explosives is achieved.

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(1) Timoshenko, "Theory of Elasticity," McGraw-Hill, New York, N.Y., 1934, p 282.

(2) M. P. Murgai, Journal of Chem. Physics, 22, 1687-1688, (1954); ibid, 25, 762-767, (1956).

Comments Submitted After the Symposium
by D. N. Griffin
Olin Mathieson Chemical Corporation

The following comments are directed towards the two papers by
Tait and Cuddy of Wyandotte Chemicals Corporation entitled "Desensiti-
zation of Liquid Monopropellants to Adiabatic Air Compression Impact
by the Addition of Ethylene Oxide," and "An Adiabatic Air Compression
Drop Weight Tester for Liquid Monopropellants" (pages 81 to 100,
Volume 2, PFL 212/13).

The drop weight tester described in their papers is not a
modification of the Bureau of Mines drop weight tester as claimed by
the authors, but is instead an early model of a drop weight tester
developed by Olin Mathieson Chemical Corporation which has become known
as the "O-Ring-Type Drop-Weight Tester." Because of that fact, and
furthermore, because Cuddy refers to the Olin-Mathieson tester as being
unsatisfactory, I consider it necessary to discuss the current status
of Olin Mathieson's work in this field.

In 1953, since we were aware of the inadequacies of most
liquid propellant impact testers then in use, Mathieson Chemical Cor-
poration undertook to develop, at Company expense, an impact tester
designed specifically for liquid propellants and explosives. With the
formation of the Committee on Test Methods for Liquid Monopropellants
we offered to coordinate our efforts with the objectives of that
committee.

At the second meeting of the Monopropellant Committee, in
February 1954, a working sub-committee was formed consisting of repre-
sentatives from Buffalo Electrochemical Company and Mathieson Chemical
Corporation and charged with recommending suitable modifications to the
ICC impact tester. For several months the sub-committee investigated
modifications of the ICC tester, none of which proved satisfactory.

At the fifth meeting of the Monopropellant Committee in
September 1954, Mr. J. W. Orr of Olin Mathieson presented his novel
idea for using a standard O-ring both to form the cup containing the
propellant sample and to act as a seal to confine the pressure developed
within the apparatus. This new drop weight apparatus, and the prelim-
inary results obtained with it, were received with interest by the
committee, and several committee members, including Wyandotte's

representative, offered to evaluate it. Consequently, copies of
Olin Mathieson's preliminary design were sent to all members of the
Committee, and Figure 1 of Cuddy's paper is a reproduction of that
drawing.

Several later modifications of this design were tested by
Mathieson including some with "cavity pistons" similar to the one used
by Cuddy in his work. Late in 1955, a modification was suggested by
members of the Explosive Research & Development Establishment in the
United Kingdom which involved placing the vent hole in the piston
rather than in the body of the apparatus. A revised design of the
Mathieson O-Ring Tester was made immediately incorporating this
suggested revision since we felt this change resulted in a significant
improvement in both the apparatus and its operation. In April 1956,
copies of this new design were submitted to the Committee.

During the past year at Olin Mathieson, we have completed
the development of this design and consider the apparatus to be satis-
factory, (cf accompanying figure). However, it has been our contention
that the operating procedures and the interpretation of data are of
even greater significance than the detailed design of the apparatus
itself. In recent months we have been completing the development of a
test method for liquid propellants and explosives, and it has been our
belief that the interests of everyone concerned, particularly potential
users, would be served best by our not releasing the apparatus design
until the complete and detailed method of operation and interpretation
of results can also be described.

In his paper, Cuddy does not indicate that Wyandotte has made
any basic changes in the design of the Olin Mathieson drop weight
tester. However, his test method does differ considerably from that
which we are developing. In Cuddy's method, rupturing of a metal
disk is not considered as an essential indication of explosion.
Instead, his "criteria of positive ignition are the absence of liquid,
presence of carbon, and disintegration of the O-ring." In the Olin
Mathieson method, rupturing of the disk (accompanied by a loud report)
has always been considered as the only positive indication of explosion.

Using a 5-lb weight, Cuddy reports values of the "50%-point"
for normal propyl nitrate varying anywhere from 7.75 to 15.6 inches,
although he emphasizes the precision of each group of tests. Using the
apparatus shown in the accompanying figure, and also with a 5-lb weight,
we have obtained a frequency of explosions of normal propyl nitrate
with a drop height of only one inch, which is equivalent to approximate-
ly one tenth of the delivered energy necessary to produce a "positive
test" in his method. We attribute this difference to the ability of
the O-ring seal to withstand extreme pressures without leakage when
proper equipment design and operating procedures are employed.

In conclusion, it should be mentioned that the information given in these remarks has all been reported to the Monopropellant Test Committee; however, the opinions expressed do not necessarily coincide with the opinions of all members of that Committee.
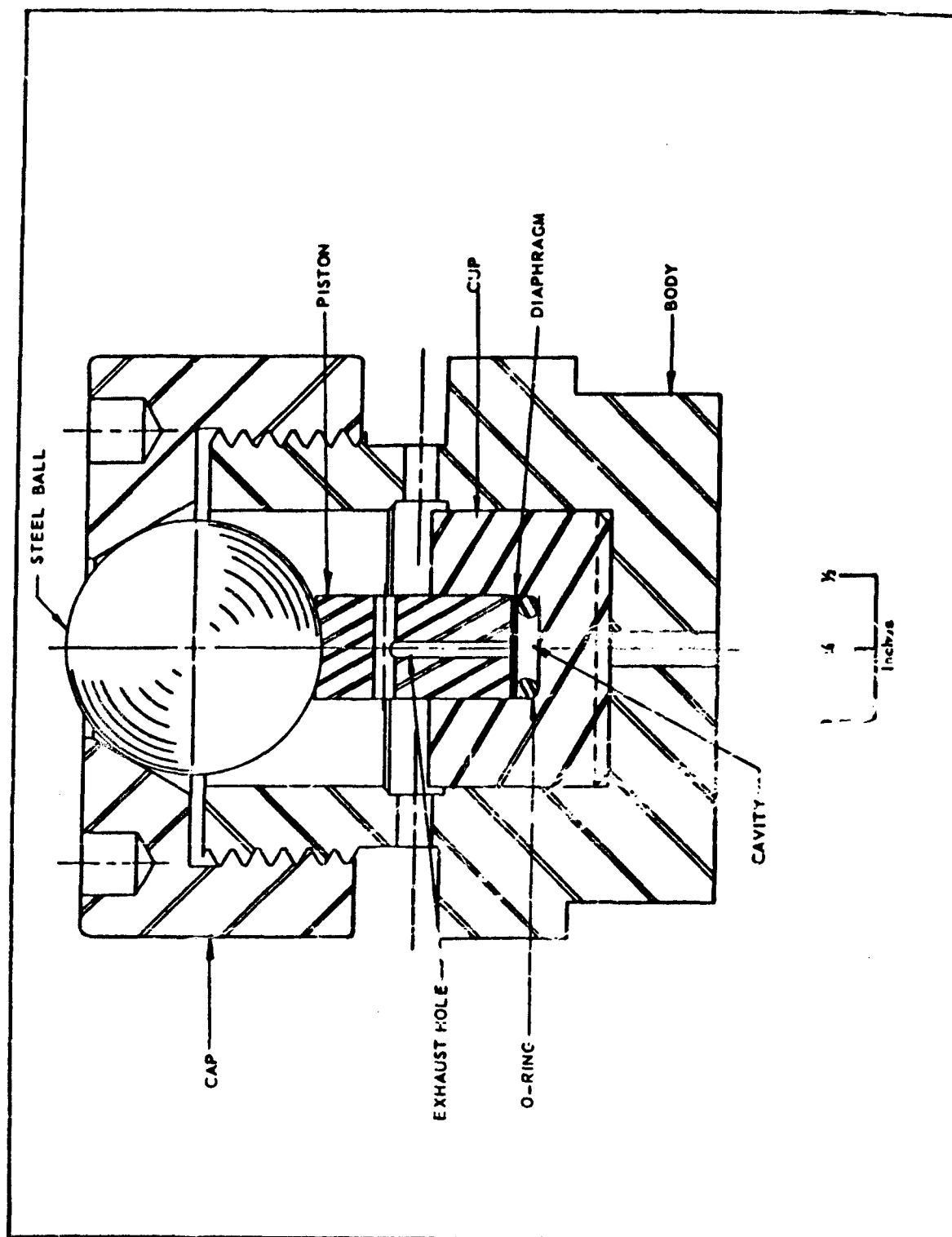
OLIN MATHIESON "O-RING-TYPE" DROP WEIGHT TESTER

Comments Submitted After the Symposium
by W. B. Moen
Air Reduction Company, Inc.

Following are comments on the paper, "Adiabatic Air Compression Drop-Weight Tester for Liquid Monopropellants," by W. A. Cuddy Wyandotte Chemicals Corporation. (Pages 81 to 100, Volume 2, PFL 212/13).

Mr. Cuddy should be commended for his presentation of results with a particular drop-weight tester applied to a single class of liquid monopropellants. The information should add appreciably to the consideration of the interdependent variables that lead to the interpretation of results derived from a test that at first seems elementary in both construction and ease of use.

Fortunately, during the past few years I have had an opportunity to follow the progress of Mr. Cuddy's program as a member of the Committee on Monopropellant Test Methods, and also to be associated with similar type test work on a program designed to evaluate the handling properties of acetylenic monopropellants. With this introduction, there follow a few comments on Mr. Cuddy's presentation.

1. Reported to the Committee on Monopropellant Test Methods have been two types of O-ring testers. Mr. Cuddy has adequately described his unit. On the other hand, the Olin Mathieson unit described in the paper has been discarded by both Wyandotte and Olin Mathieson for the reasons enumerated. However, the Olin Mathieson unit has been revised, and this revised unit is now in use at Olin Mathieson, Air Reduction, and Army Ballistic Missile Agency.

This revised O-ring tester differs from that shown in figure 1 of Mr. Cuddy's paper in one major respect; that is, the bottom of the test cavity is not vented, and instead a diaphragm is placed on top of the O-ring. When a reaction ensues, venting takes place through a hole in the piston. This modification has overcome to a great extent the three objections raised by Mr. Cuddy to the first O-ring tester used.

It is believed that the results obtained with both testers on the materials tested -- that is the alkyl nitrates -- are comparable. The results on both testers were obtained by utilizing the so-called "ladder" technique.

54

2. The data reported by Mr. Cuddy have been obtained by maintaining a constant liquid volume, and the bubble size is varied by varying the indent of the active piston face. Consequently, the total volume in the test cavity, including liquid and vapor, has not always remained constant. The Olin Mathieson revised tester, on the other hand, maintains under constant precompression conditions a constant total volume, and varies the liquid-vapor ratio by a careful control of the filling density. It has been found that the filling density is an important variable when other conditions remain fixed, as can be seen from figure 1. In consideration of these data, therefore, one must not indiscriminately select a filling density.

3. One may believe that he can compensate for different drop-weights used by adjusting the drop-height to give a constant potential energy in the weight at the start of the test. This has been shown not to be true (figure 2). These data were obtained with water in the test cavity, and show that the energy transmitted to the test capsule assembly is significantly different as the drop-weight is changed. Apparently the velocity being independent of weight has an important effect on the amount of energy transmitted to the cavity. Conceivably, it would be preferred to compensate for different drop-weights by assuming a constant momentum input as the drop-weight is changed. Of course the reflections of the energy within the test capsule assembly will be changed with different velocities and weights. Mr. Cuddy was aware of some of these effects.

4. It has been determined at Airco that the gap between the O-ring and the blow-out disc during reaction is extremely critical. In an effort to obtain a satisfactory seal, the effect of precompression was investigated. It has been found that above a critical precompression value, using a system with well lubricated o-rings, 10 in-lbs torque gives very satisfactory results with IBM as the test fuel (0.03 cc liquid sample, 0.0153" thick diaphragm, 5 lb weight) and only a 2" drop-height is required. On the other hand, with no pre-compression except that imposed by the tare of the free parts of the capsule assembly, a drop-height of 5 in-lbs is required. Furthermore, with the higher torque value mentioned, the reproducibility of the results is increased.

We have also found that by using a precompressed O-ring, the effect of the varying weight of different O-rings virtually drops out as a significant parameter. One may argue that the ullage varies as the weight of the O-ring changes even though a constant precompres-sion is used; however, it is believed that this is insignificant when one considers the extremely small changes in volume that can result if constant density O-rings are assumed over the range of the O-ring weights used.

5. If one considers the O-ring weight as a variable, as has been done by Mr. Cuddy, it is only an indication of some other O-ring factor change such as a variation in the O-ring torus cross-section

and its effect on filling density or liquid vapor ratio, as well as the durometer variation due to rubber density change.

In this connection, also, Mr. Cuddy mentions that normal variations in ambient temperature do not significantly affect the results, and proves this by calculating the adiabatic compression temperature for moderate variations of ambient temperature. What he does not show, however, is the effect on durometer with temperature which would determine the proportion of energy absorbed by the O-ring at different temperatures. It is believed from our work that precompression virtually cancels this last effect.

6. It is unfortunate that all three organizations, Olin Mathieson, Wyandotte, and Airco have so far reported extensive results on only one class of compound, the alkyl nitrates. Both the Wyandotte and the revised Olin Mathieson versions of the O-ring tester appear to produce reasonably good results. What is not known is whether or not either tester can be extended to use on other families of materials. It is granted that the Wyandotte tester has served a very useful screening purpose as described in the paper by Tait and Cuddy entitled "Desensitization of Liquid Monopropellants to Adiabatic Air Compression Impact by the Addition of Ethylene Oxide."

From the limited experience with testing other materials such as nitromethane, hydrazine, unsymmetrical dimethylhydrazine, isopropenyl acetylene, and diisopropenyl acetylene, we have not been able to initiate decomposition of these materials at the maximum available drop-heights of 75 inches when using the same test conditions that would cause n-propyl nitrate initiation at a drop-height of 2 inches. It is agreed that materials such as the hydrazines and acetylenics are quite stable, but nitromethane is known for its sensitivity to adiabatic compression activation. From our statement, one then can question the universal use of the tester in comparing many materials, without varying some of the test parameters.

7. Mr. Cuddy mentions the effect of initial temperature and relative humidity on the adiabatic compression sensitivity, and concludes that under normal ambient initial conditions for a material with a weak vapor pressure, temperature dependence would not be significant. When one considers such materials as n-propyl nitrate or nitromethane with relatively low vapor pressures, the fuel-air mixture ratio in the vapor space is not too far above the lower flammability limit. Consequently, if one wishes to ignite these materials at their auto-decomposition temperature, one must hold this temperature for at least the induction period which, of course, is relatively long as compared with that required for stoichiometric mixtures. In the drop-weight tester, such a temperature cannot be held for any length of time; and if one wishes to initiate decomposition in a drop-weight tester, the adiabatic compression temperature must be well above the autodecomposition temperature, and the time for holding the vapor above the autodecomposition temperature above the liquid must be sufficiently

long. Perhaps this explains why nitromethane appears to be more difficult to ignite than any n-propyl nitrate.

8. It is unfortunate that Mr. Cuddy did not include the results from both Olin Mathieson and Airco on n-propyl nitrate for the two different testers. It is believed that sufficient data do not yet exist to regard the Wyandotte tester as one that can be recommended for use by anyone. However, his paper should be regarded as a valuable contribution as a progress report on the development of an ultimate tester. In this connection, as Chairman of the Committee on Monopropellant Test Methods, I would like to caution anyone considering such a tester that the Committee has not yet recommended any tester for general use at this time. It is actively reviewing all past and current work, and hopes within the near future to come up with preferred equipment and procedures. In this connection it should be mentioned that Dr. Tschinkel of the Army Ballistic Missile Agency has both types of testers and is running the same materials in both testers. The results of his work should be of value to the Committee in their selection of a preferred tester. Whether the Wyandotte unit is selected by the Committee remains to be seen.
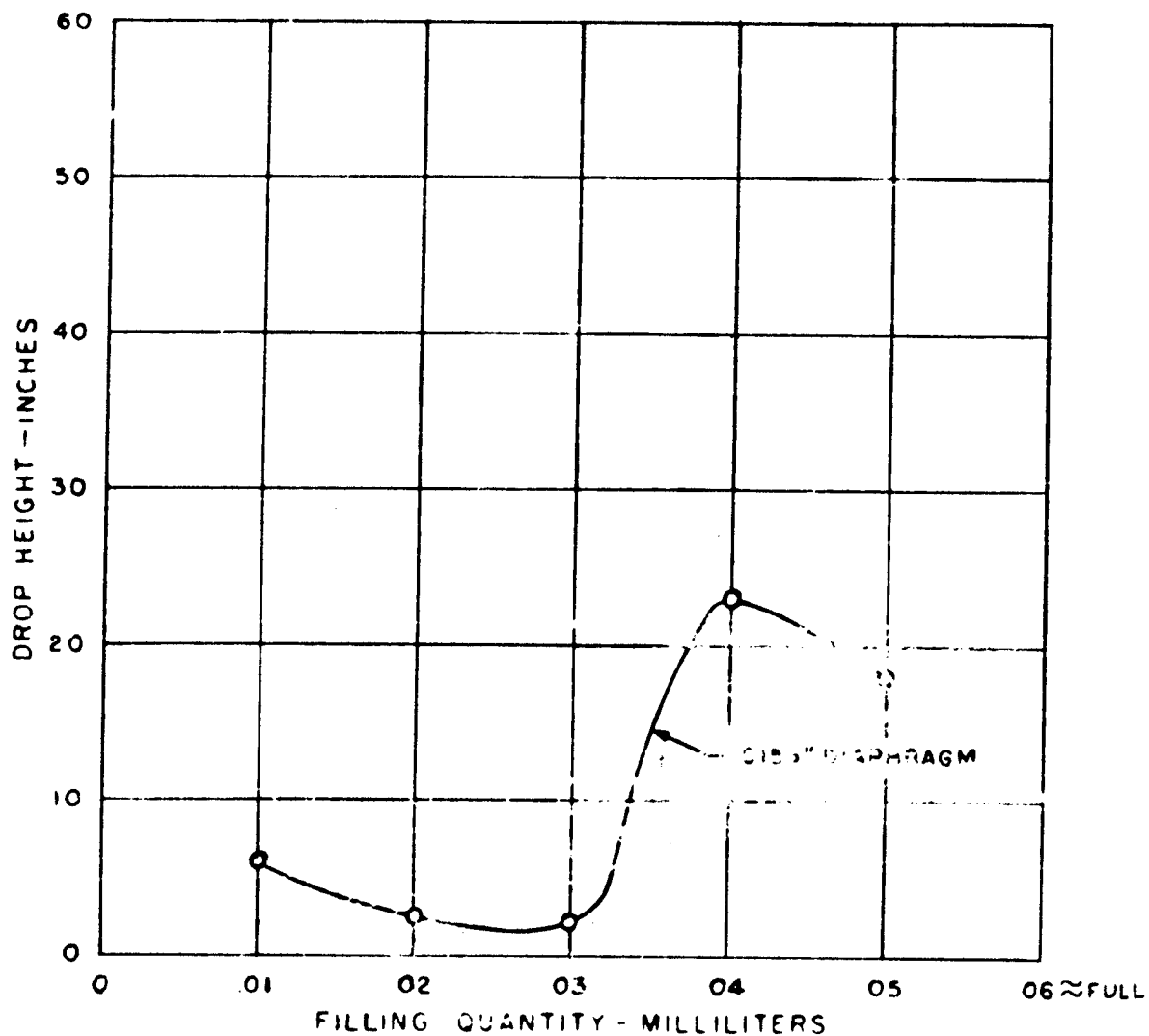
DROP HEIGHT SENSITIVITY VS FILLING
QUANTITY OF N-PROPYL NITRATE
(DROP WEIGHT = 50 POUNDS)

Figure 1

58

Figure 2
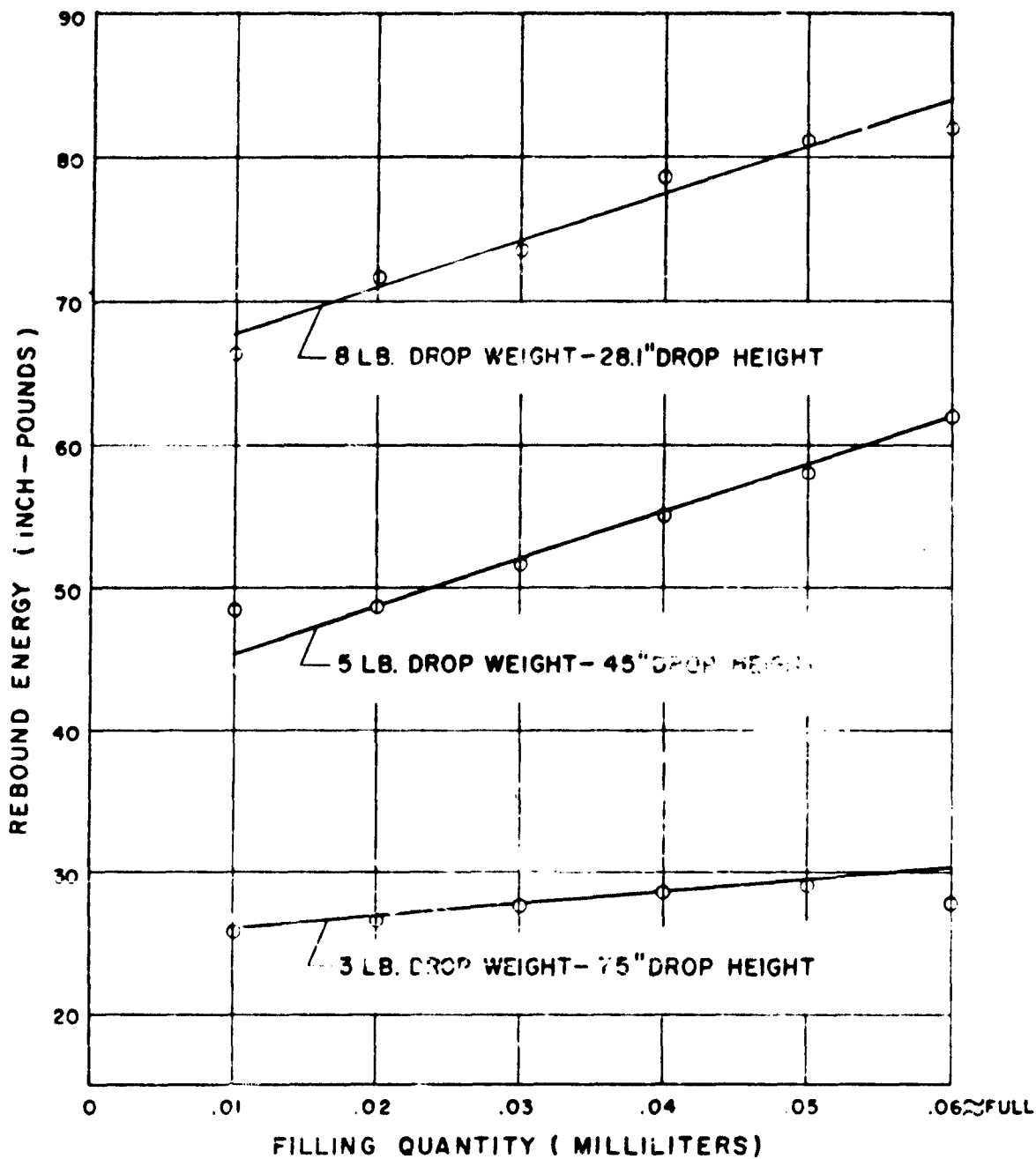
ELASTICITY OF IMPACT
VS.
FILLING QUANTITY AND DROP WEIGHT
(POTENTIAL ENERGY = CONSTANT = 225 INCH-POUNDS)

28 MARCH 1957
MORNING SESSION

CHAIRMAN: MR. J. F. TORMEY

PAPER

EFFECT OF HYDROCARBON FUEL COMPOSITION ON ROCKET PERFORMANCE

by Jacob Silverman & Robert J. Thompson
(Presented by Dr. Thompson)
Rocketdyne, A Division of North American Aviation, Inc.

(See pages 150 to 191, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by W. P. Knight
Aerojet-General Corporation

(See following pages 61 to 73)

Discussion Prepared by
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on Jacob Silverman - Robert J. Thompson Paper
EFFECT OF HYDROCARBON FUEL COMPOSITION ON ROCKET PERFORMANCE

I.   INTRODUCTION

The subject of the paper presented by Rocketdyne is one of extreme interest, and has, for a considerable period of time, been the object of concern of rocket engineers and propellant chemists involved in the use of hydrocarbon fuels. No less interested have been the various agencies of the armed services who must consider the logistics problem, and the members of the petroleum industry who must supply the material. This subject, the effect of hydrocarbon fuel composition on rocket performance, is of special interest to the Aerojet-General Corporation because of a program of similar nature, although of much lesser magnitude, in which they have been engaged for some time—the Referee Grade JP-4 Fuel Program.

This program does not encompass any work with gas generators, but from studies on other projects, both experimental and theoretical, indications are that aromatic constituents are undesirable in fuel rich gas generators. Because of the lower heating value and higher carbon-to-hydrogen ratio of these species, the performance will suffer and carbon formation is enhanced. This would be an especially important factor for use in long-range ballistic missiles.

As to the performance in a thrust chamber, however, Aerojet has not found on this program that the composition of the fuel has any significant effect.

Time does not permit here a detailed discussion of the work conducted at Aerojet but the salient points of this project and a few illustrative results will be presented. Another paper on this subject, by J. N. Barger and H. B. Ellis of Aerojet, will be included in the published proceedings of this symposium and may be referred to for additional information.

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II. BRIEF SUMMARY OF PURPOSE OF REFEREE JP-4 FUEL PROGRAM

    A. OBJECTIVE

        The objective of this program was to establish a "referee" grade of JP-4 fuel representing the fuel composition which would be the most unreliable in a rocket engine, yet remain within the specifications set forth in MIL-F-5624C.

    B. REVIEW OF PROGRAM

        The program is outlined as follows: By mutual agreement between the Wright Air Development Center and the Aerojet-General Corporation, eight formulations of JP-4 rocket fuels were selected, and the Universal Oil Products Company was requested to blend, analyze, and ship the fuels to Aerojet for evaluation. These formulations were chosen to represent variations in the aromatic, olefinic, naphthenic, isoparaffinic, and normal paraffinic content as wide as might be expected during war or peace-time production. The formulations were held within the limits of Specification MIL-F-5624C, except for Blends No. 7 and No. 8, in which the olefin content was increased to 15 and 20%, respectively, because the specification limit of 5% would not allow sufficient variation to delineate the effects of olefin concentration.

    The Universal Oil Products Company provided, with the fuels, a detailed analysis. A summary of the composition of the eight blends is reproduced herein as Table I.

    Each of the eight blends was to be evaluated in the laboratory and in thrust chambers. The laboratory phase of the evaluation comprises the measurement of the properties and the determination of the combustion behavior which might be expected to influence rocket-engine performance. The fuels were to be burned in thrust chambers with IRFNA and oxygen at various thrust levels. Attempts were to be made to correlate statistically the chemical properties and the composition of the fuel with thrust-chamber performance, operational performance, operational stability, and starting and shutdown characteristics. Employing these correlations, the worst concentration of each component that is variable within military specifications was to be established, and an especially doctored "worst" blend was to be formulated and test-fired.

    Each of the eight special JP-4 blends were to be test-fired according to a schedule in which the fuels were to be evaluated with IRFNA and oxygen at various thrust levels.

    An Aerojet-General 50-lb-thrust starter motor was employed to determine the following properties:

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Knight

1. The minimum glow-plug temperature required to ignite each blend with IRFNA as a function of mixture ratio in the range from 2.5 to 6.0.

2. The minimum spark energy required to ignite each blend and gaseous oxygen at the optimum mixture ratio.

3. Ignition delay as a function of mixture ratio and glow-plug temperature (with IRFNA) and spark energy (with oxygen).

4. Characteristic velocity, c^*, for each test firing.

Each fuel was to be fired with IRFNA and oxygen in a 5000-lb thrust chamber to determine the following:

1. Starting characteristics
2. Steady-state combustion characteristics
3. Operational stability
4. Shutdown characteristics.

The thrust-chamber chosen for this work was an LR-63 type, developing 5000-lb of thrust at a chamber pressure of 385 psia. This chamber is stable in operation, rugged in construction, end has been qualified for use on aircraft. A large back-log of information from previous test-firings was also available. The L* of this chamber is 48 in. and it has a contraction ratio of 3:1.

In order to study the operational stability, the thrust chamber was equipped with a pulsing unit. This unit will initiate pressure oscillations in the thrust chamber by suddenly introducing a surge of fuel amounting to a 10 to 100% increase in fuel-flow rate for a period of from 3 to 5 millisec. The surge in chamber pressure provides oscillations, the nature of which should be indicative of the inherent stability of the propellant combination. The time required for the resumption of steady-state operation, the amplitude of the pressure surge, and the frequency of the induced combustion-instability waves are to be measured.

The "best" and "worst" blends, as indicated by a statistical analysis of the data, were to be spot-checked by test firings at thrust levels other than 50 and 5000-lb. In addition, a special blend was to be formulated in which each component would be present, insofar as possible, in the amount which was shown to be most detrimental to stable operation. This "doctored" blend was to be fired with IRFNA and LOX at the thrust levels employed to test the eight special blends.

III. RESULTS

A. STARTER MOTOR

1. Minimum Glow-Plug Temperature Required for Ignition with IRFNA

The minimum glow-plug temperature required for ignition with IRFNA was determined as a function of mixture ratio from 2.75 to 6.0. Because the larger thrust unit was operated at a mixture ratio of 4.0, only the results obtained at that mixture ratio will be reported here. As may be noted in Table II, the eight special blends all ignited in the range from 1100 to 1400°F, a spread of 300°F.

2. Ignition Delay with IRFNA

The ignition was measured as a function of glow-plug temperature and mixture ratio. The ignition delay for each blend decreased with increased glow-plug temperature up to 1800°F, at which point the ignition delay became essentially constant with increasing glow-plug temperature. Table III shows the ignition delay at 1400 and 1800°F for each blend at MR = 4.0. At 1800°F the ignition delays for all eight blends were within 6 millisec, from 8 to 14. In other words, the ignition delay for all eight blends at 1800°F was 10 ± 3 millisec.

3. Minimum Primary Spark Voltage for Ignition with Gaseous Oxygen

With oxygen as the oxidizer, an automotive spark plug was utilized to obtain ignition. The energy of the spark was controlled by varying the voltage input to the primary coil. Two distinct energy levels were found, one being the minimum primary voltage required to obtain any ignition, and the second, higher voltage which gave ignition with a delay reproducible to ± 1 millisec. Table IV illustrates these energy levels for the eight fuel blends at MR = 2.3 and the ignition delay at the reproducible level. Between the two voltage levels, the ignition delays varied greatly and were not reproducible in any manner. At 135 volts input, all blends ignited between 5 and 13 millisec.

B. 5000-lb THRUST CHAMBER

1. Starting and Shutdown Characteristics

Ignition in the thrust chamber was accomplished by means of a starter motor of the type which has just been described. As far as ignition characteristics in the main chamber were concerned, the difference from one blend to another was no greater than differences observed in replicate tests with the same blend. The small differences which did exist in the starting transients were as bable to variations in valve opening times and transients in the recording instruments. The same held true for the shutdown characteristics.

2. Operational Stability

a. The analysis of tests at steady-state operation, 385 psia chamber pressure at a mixture ratio of 4.0, indicated no significant changes in chamber pressure variations. In other words,

there was no tendency exhibited by any of the fuels toward combustion instability.

        b.   When the fuel pulse was utilized in an attempt to induce combustion instability with IRFNA, the chamber pressure increased rapidly to a peak which varied with the different fuels from 391 to 517 psia. The total time required for the chamber to return to normal steady-state operation varied from 28 to 70 millisec. These times were reproducible on subsequent runs to ± 3 millisec. Although the values of these parameters vary substantially from one blend to another, they are not considered to be significant in the operation of the thrust chamber, because the recovery time in all cases was actually extremely short.

        c.   The data for the liquid oxygen tests have not been totally reduced as yet. However, it may be stated that steady-state combustion efficiency and stability show only minor variations between blends.

3. Performance

        The information available on performance of the fuels at this writing does not include the experimental values for the liquid oxygen tests. These data are currently being reduced, and it is hoped that the figures will be available in time to report at the symposium.

        a.   Specific Impulse

        The theoretical specific impulse was calculated for each blend under conditions of both frozen and shifting equilibrium. The performance with IRFNA was calculated over a mixture ratio range from 2.5 to 5.5 and with LOX over the range from 1.5 to 3.5. All the calculated impulses were for a chamber pressure of 300 psia and an exhaust pressure of 14.7 psia.

        Table V presents both the experimental and theoretical values of I_{sp} with IRFNA at the MR employed in the 5000-lb thrust chamber. It is to be noted that the maximum difference in the calculated I_{sp} among the blends is 2 seconds of impulse, ranging from 228 to 230 lb-sec/lb. These differences are well within the 1.5% error which is inherent in the thermodynamic data used to perform the calculations. It may therefore be stated that there exists no difference in the theoretical performance among the eight fuels. The values for the experimental specific impulse vary from 197 to 208 lb-sec/lb. At first glance this appears as if it might be significant; however, the calculated standard deviation is only 1.5%, yielding a mean experimental specific impulse for the eight blends of 203.4 ± 3.5 lb-sec/lb. This again is within both the experimental and theoretical error.

        b.   Characteristic Velocity

        The c^{*} values for the eight blends were calculated

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for shifting and frozen equilibrium with both oxidizers, and over the
same mixture ratio ranges as were the specific impulses. Table VI
shows the experimental and theoretical values with IRFNA at a mixture
ratio of 4.0. As may be seen, the calculated c^* values with IRFNA
from the highest to the lowest varied only 48 ft/sec, not enough
difference to distinguish between blends. The greatest variation in
experimental c^* values was 116 ft/sec. The standard deviation com-
puted for the experimental values of c^* of the eight blends is equal
to 0.74%, or ± 36 ft/sec. The mean c^* is therefore 4,602 ± 36 ft/sec.
Because the measurement of c^* in this apparatus was reproducible to
± 40 ft/sec, it is obvious that no differences in the 8 blends existed.

IV. CONCLUSIONS

A. STATISTICAL ANALYSIS

The services of the Quality Assurance Division of Aerojet-
General Corporation have been utilized from the inception of the
Referee Fuel Program to set up the test program in such a manner as to
provide the most meaningful data insofar as possible within the scope
of the contract. As a result, the chemical, physical and combustion
properties of the eight special JP-4 fuel blends have been analyzed
statistically for correlation among the various sets of data, and this
information used in forming the conclusions reached to date.

B. STARTER MOTOR

The conclusion drawn from the ignition tests is that any
JP-4 within the limits of MIL-F-5624C will ignite satisfactorily with
IRFNA at sea level pressure and room temperature conditions in an
Aerojet starter motor at a glow-plug temperature of 1200°F or higher,
and with gaseous oxygen at a minimum of voltage of 125 volts for
the spark plug.

C. 5000-lb THRUST CHAMBER

It was concluded from the tests conducted on this program
that a fully developed thrust chamber, such as was utilized, will
start, run, and shutdown satisfactorily using a wide variation in JP-4
fuels. There were insufficient differences noted in the operational
characteristics of the fuel blends in this engine to conclude that any
particular composition was inferior to any other.

V. ADDITIONAL REMARKS

Because of the conclusions that no "worst blend" was evident
among the hydrocarbon fuels tested, no special composition embodying
the undesirable constituents of JP-4 is possible. In lieu of formu-
lating and testing such a fuel, Aerojet-General Corporation will test
the eight JP-4 blends in a thrust chamber of 15-in. diameter, operating
at the 7,500-lb thrust level. In addition to the fuel pulse, a tan-

CONFIDENTIAL

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gential mode of high frequency instability will be induced. Because large rocket engines are frequently subject to such instability characteristics it is believed that the data will be useful in applying the performance characteristics of the varied JP-4 compositions to very large thrust chambers, thus reducing the amount of extrapolation of data from smaller thrust chambers that is necessary at the present time.

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TABLE I

SUMMARIZED ANALYSIS OF THE SPECIAL JP-4 BLENDS

	Blend No., (Volume %)							
	1	2	3	4	5	6	7	8
Normal paraffins	62.62	16.67	7.45	53.93	0.07	2.60	20.25	0.05
Branched paraffins	14.05	77.24	11.24	7.16	74.93	11.53	27.71	54.95
Olefins	—	—	—	—	—	—	15.00	20.00
Naphthenes	19.93	0.53	74.76	13.49	—	62.07	24.09	—
Aromatics	4.40	5.41	6.55	25.42	25.00	23.80	12.95	25.00

TABLE II

MINIMUM GLOW-PLUG TEMPERATURE REQUIRED FOR IGNITION
IN STARTER MOTOR WITH IRFNA

MR = 4.0

Blend No.	1	1400°F
	2	1200
	3	1300
	4	1100
	5	1200
	6	1200
	7	1300
	8	1300

TABLE III

IGNITION DELAY IN STARTER MOTOR WITH IRFNA

MR = 4.0

Glow-Plug Temp.	1400°F	1800°F
Blend No. 1	19 Millisec	13 Millisec
2	16	14
3	13	11
4	11	9
5	10	8
6	~7	~~
7	11	8
8	17	~

TABLE IV

IGNITION DELAY IN STARTER MOTOR WITH GASEOUS OXYGEN

MR = 2.3

Blend No.	Minimum Voltage For Ignition (Volts)	Minimum Voltage For Reproducible Ignition (Volts)	Ignition Delay at Voltage for Reproducible Ignition (Millisec)
1	90	110	11
2	45	110	7
3	90	110	10
4	75	120	8
5	9	110	6
6	45	130	7
7	35	130	12
8	65	130	9

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<u>TABLE V</u>

EXPERIMENTAL AND THEORETICAL I_{sp} WITH IRFNA

MR = 4.0, P_c = 385 PSIA

BLEND NO.	EXPERIMENTAL I_{sp} (LB SEC/LB)	THEORETICAL MOBILE EQUILIBRIUM I_{sp} (LB SEC/LB)	THEORETICAL FROZEN EQUILIBRIUM I_{sp} (LB SEC/LB)
1	207	230	227
2	203	229	226
3	207	229	226
4	197	229	226
5	203	228	225
6	208	230	226
7	200	229	226
8	202	229	226

CONFIDENTIAL

Knight

TABLE VI

EXPERIMENTAL AND THEORETICAL c* WITH IRFNA

MR = 4.0, P_c = 385 psia

Blend No.	Experimental c* (ft/sec)	Theoretical Mobile Equilibrium c* (ft/sec)	Theoretical Frozen Equilibrium c* (ft/sec)
1	4850	5082	5053
2	4583	5054	5029
3	4663	5043	5012
4	4767	5048	5016
5	4605	5034	5004
6	4656	5060	5024
7	4553	5056	5025
8	4597	5038	5002

GENERAL DISCUSSION

P. D. CAESAR (Socony Mobil Oil Company, Inc.): I have a couple of points on Dr. Thompson's paper that I would like to make. First, I would like to read one passage in his paper that has worried me quite a bit. He states: "Within the limitations of the extensive chemical analyses of Table III (and they are quite extensive, some five pages worth) the standard thinner fuel is in all respects equivalent to the JP-5R and like JP-5R meets the specification requirements of RP-1. Yet its performance is distinctly lower."

There is, however, one significant difference in the properties of those two fuels. The ratio of CH_2 to CH_3, in other words, the degree of chain branching, in the JP-5R, is twice that of the standard thinner. Now this may not seem to be a critical difference, but if you look at fuels in other combustion systems, you realize the effect that molecular structure has on the combustion properties of saturated hydrocarbons. I refer to gasoline in particular. This difference in CH_2/CH_3 ratio is a very concrete difference. I am not at all surprised (by analogy) that it affects some combustion characteristic of jet fuels.

I would like to stress one more thing with a word of caution. It is a great temptation on the basis of experimental and theoretical evidence to make specifications that possibly can be met in time of peace, but are very tough to meet in national emergencies, when you really need these fuels in large quantities. It may seem very easy on paper to knock down the aromatic content from 15 to 5 percent. It can probably be done in many refineries in peacetime. But in a national emergency this might be very tough to realize.

DR. THOMPSON: I will comment briefly on Mr. Caesar's two points here.

Taking the second point first, I was very aware of this and we wrestled many hours with the economies that have to be made between optimum desirability and optimum availability. We would like to have more. We didn't try to go quite that far for this particular application. I don't think this is the place to get into logistic discussions. For this particular application, which is for the larger rocket engines for the ballistic missiles, the requirements are not anything comparable to those for, let's say, operational aircraft. Each one of these things just flies once and so we are not really talking about a vast quantity of material even in time of emergency in the sense that one thinks of a more conventional aircraft fuel.

And the first point, I think, is very well taken. We had given some consideration to that chain branching effect. Perhaps it would have been better to say that this illustrates a rather fine type of difference that you are not going to get out of the ASTM

specification and indicates that there may be significant differences due to a rather fine point of structure that is not going to be easily detectable by the normal specification tests.

M. J. ZUCROW (Purdue University): I would like to ask Dr. Thompson two questions. One, what is the L* you assumed for the fuels; two, what do you think the results would be if you had investigated fuels at different values of L*?

DR. THOMPSON: On the first one, I would say it isn't as low as we tested and these motors get, but the tendency is downward. Certainly we did deliberately choose low L* trying to accentuate differences within the limitations of instrumentation for the relatively small motors in the 2500 to 300,000 pound thrust range. It is pretty hard to find things which are below 1% and 1-1/2%. Even at this L* the differences, for example, between the normal paraffins and the aromatics presented to us are pretty close to what you calculated, so that we gained some confidence. I don't know what this proved necessarily, but it is comforting to see that they came in the same order as one would calculate.

I think the thing that you have to remember is that in the large engines for ballistic missiles we are struggling to get a degree of precision and accuracy in rocketry that nobody even worried about before. Admittedly our present instrumentation isn't really good enough in all cases to detect the differences which we know ultimately will be important, but we ought to meet the variations well below 1% if we are going to make things reasonably easy for the people who have to worry about guidance mixture ratio control, cut-off, and so forth. A 1% difference in performance imposes quite a strain on the rest of the systems.

MR. KNAPP: I have one question for each speaker. The first one for Dr. Thompson, I think, is somewhat related to Dr. Zucrow's question. If the data were reported in terms of theoretical performance, I might be less confused. If theoretical calculations are made on the performance of hydrocarbons, I would appreciate a difference in performance between paraffin and aromatics depending on their heats of formation. Lacking these data I am unable to tell whether the difference in the experimental performance is due to combustion efficiency or merely due to the thermodynamics of the system. Bob can perhaps answer this question for me: Was there a decided difference between the combustion efficiencies of the various hydrocarbon systems?

The second question is for Mr. Knight, and I must admit it's sort of a dirty question. I think most of you here are aware of my previous work. We found considerable difference in the performance characteristics, in this case combustion stability, depending on the aromatic content of the various fractions in JP fuel systems. As I interpret Bill's statements, in their engine there was no appreciable difference with combustion stability characteristics of any of the JP

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fuels they tested -- and this is the dirty part of my question -- if this is true, how does one interpret the difficulty encountered in the acid-JP-4 system in an engine such as BOMARC particularly in respect to the method used in solving the problem?

DR. THOMPSON: On your first question, I did not take time to explain just how these data were arrived at. I think it is explained in the text. Everything was reduced to the basis of common pressure and expansion ratio. They are all compared at 500 psi, and the expansion ratio, that I don't remember, but it is consistent throughout. We were more interested in the real differences than in the percentage of the theoretical differences. However, at the 5-inch L* I think it is obvious that these things did not line up thermodynamically -- the olefins in some cases had a high combustion efficiency, pretty near infinity, down to the materials like the heavy alkylate which was perhaps on the order of 85%.

Now the 20-inch L* - these things end out remarkably well. I think almost all the combustion efficiencies could be characterized as 96 ± 1%. They were surprisingly consistent in the combustion efficiency compared to theoretical calculations for all the fuels tested.

MR. KNIGHT: I have not been particularly close to the problem of combustion stability in the BOMARC. However, I do know they have found mechanical problems in the system which was leading to part of this instability. I understand there have been indications recently of having some low frequency instability, but I have no confirmation of this, nor any information as to what might be the cause.

We are also planning to try some high frequency instability on these JP-4 blends. You will hear a paper later by Mr. Ellis of Aerojet who will describe some of his work along this line. This study will include our eight blends so that we will have some high frequency instability data on them. This is a relatively low frequency instability induced by the pulse which I just described and we hope to find some differences among the blends with our high frequency technique.

CONFIDENTIAL

76

PAPER

THE PERFORMANCE OF UNSYM-DIMETHYLHYDRAZINE-RED NITRIC ACID
IN A MOTOR AT VARYING THRUST LEVELS

by N. J. Sippel, D. H. Couch, Stanley Singer
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PREPARED DISCUSSION

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Discussion Prepared by
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on N. J. Sippel, D. H. Couch, Stanley Singer Paper
THE PERFORMANCE OF UNSYM-DIMETHYLHYDRAZINE-RED NITRIC ACID
IN A MOTOR AT VARYING THRUST LEVELS

The contributions made by the NOTS, in the course of the
IAR program, to the high pressure, high performance, high loading den-
sity rocket motor with nitric acid propellants are well known. In the
present paper, the authors have made a further useful contribution by
exploring, initially at least, the subject of variable thrust with
fixed injection in this type of rocket motor operating on RFNA/UDMH.

The results of the work raise some interesting questions.
First, why does c^* drop off so sharply below about the 50 psi chamber
pressure level? Is it a result of some critical hydrodynamic affect
in injection? Or is it a result of some sharp pressure dependency of
burning rate of the propellant combination? Is it feasible to design
high frequency combustion instability into the low-chamber-pressure
regime so as to raise combustion efficiency therein while avoiding the
more destructive combustion instability in the high chamber pressure
regime? The answers to such questions can give additional means for
achieving high c^* at low pressure.

Second, what is the source of the scatter in some of the
c^*'s in the higher chamber pressure range? If due to the use of pres-
sure averages, can it be properly reduced by a more refined weighting
of the data? Or does the determining of true effective chamber pres-
sure require a different measuring technique? Is the scatter instead
due to actual differences in injection and combustion conditions be-
tween runs made under nominally identical design and operating condi-
tions? If so, what actually accounts for these differences and what
remedy can be applied to yield the reproducibility of c^* desired for a
missile application?

We can be sure that these questions have been asked by the
authors of themselves and we can expect that further investigations
into them may be reported at future meetings.

GENERAL DISCUSSION

DR. SINGER: Many additional thrust level tests have been made with the PEMLAR since the results reported in the preprints of this Symposium. Several new factors which markedly affect performance have been noted: (1) Oxidizer-fuel ratios of 2.4 or less can lead to combustion instability, (2) At mass flow rates greater than 12.4 lb/sec C* decreases, (3) At higher propellant flow rates (greater than ca 12 lb/sec) oxidizer-fuel ratios above 2.6 decrease C* markedly although a relatively small change in loading density rate may occur. High C* as reported in a few of the tests in the paper requires careful adjustment of these factors. It appears that at the higher flow rates C*'s of 5,000 fps cannot be obtained reliably, but that lower values of ca 4,500 fps are obtainable without excessive precision in control of the factors mentioned. It may be noted that performance differences pointed out by Mr. Youngquist in "nominally duplicate" tests of Table 2 may be correlated in part with the aid of these factors.

W. L. DOYLE (Research Institute of Temple University): I have just one question. I was looking at the deflector rings. Just how much trouble do you have in cooling or melting problems, say, particularly in high-temperature regions?

DR. SINGER: We don't cool the deflector ring. This motor is cooled only around the nozzle. In certain types of combustion instability the deflector ring is eroded or melted. Now in some erosion the inner surface of the deflector ring is not attacked at all, but the outer face is eaten away; and if the test is continued long enough this erosion gradually works its way into the deflector which is in contact with the liquid.

Mr. Youngquist's suggestions were very interesting. I believe that the data we have now show we can generate high frequency combustion instability when we want to at the lower chamber pressures and lower flow rates, and perhaps increase C* by this method. I mentioned some of the factors by which this might be done by the change in the ratio, although we are not sure how delicate this adjustment has to be right now.

MR. DOYLE: I think you misunderstood my question just a little bit. I didn't mean the deflector ring cooled. You see, the question was the cooling of the ring would be by the impingement of the propellant ring. I did not mean that the ring itself cooled. That might be possible, though.

DR. SINGER: Yes, the observations on erosion just mentioned indicate that the inner surface of the ring is cooled by the propellant flow. On the deflector ring between the streams of oxidizer and fuel there are occasionally observed small lines.

DR. NOEGGERATH: I think a number of Dr. Youngquist's questions can easily be answered by examining the paper.

Having been closely associated with the original development of this injector, I can say that this injector was designed for different design conditions than the ones under which it is used now. This injector was designed to give good combustion efficiency with a small pressure drop if a core of hot gasses generated by a separate solid propellant was added. This centrally located hot flame is used to ignite and evenly distribute the propellants over the combustion chamber. In the tests presented in this paper, however, the core of hot gas was omitted and the injector had to work like any other injector. That means that it must rely on atomization of the liquid in order to obtain a good combustion efficiency and a high C* value. This, however, required a very high pressure drop because, as I said before, the injector was not designed for this condition.

If you look at the results presented in this paper in Table II you will see that one obtains high combustion efficiency only with high pressure drops. The way this injector was originally designed, one cannot get a high C* without a central igniter flame at low pressure drops. I think we have explained the results presented in this paper.

DR. SINGER: Dr. Noeggerath brought up some complex questions on which we feel we have, well, reasonable discussion if not actual answers. Our recent studies have led us to believe that the gas jet in the LAR as it is now used if applied in the small diameter PEMLAR chamber may actually cause a slight decrease in performance because the volume in the chamber is limited.

We are going to study this effect very closely and also study the liquid flow phenomena that are involved. However, the idea that the C* drops at the lower flow rates, as Dr. Noeggerath mentioned, I believe, is correct. I believe this is due to a loss in the velocity of the liquid streams which results in poorer mixing.

MR. TURPZY: The next paper departs slightly from the general theme of propellants, but it is probably of utmost importance to the entire rocket field.

PAPER

THE TANGENTIAL MODE OF COMBUSTION INSTABILITY

by R. S. Pickford & H. B. Ellis
(Presented by Dr. Ellis)
Aerojet-General Corporation

PREPARED DISCUSSION

by Jerry Grey
Princeton University

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Discussion Prepared by
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Princeton University
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on R. S. Pickford and H. B. Ellis Paper
THE TANGENTIAL MODE OF COMBUSTION INSTABILITY

The authors have described an investigation of a crucial problem which has faced the designer of large liquid-propellant rocket engines for years, and they are to be commended on the excellence and significance of their study. The paper presents quite comprehensive experimental results on the subject of tangential-mode instability, and clearly describes, for the first time, its detailed characteristics. Pickford and Ellis' analysis of their observations is direct and well-justified, and provides a complete phenomenological description of tangential instability.

The use of photographic methods in this study provided an excellent description of the wave motion occurring in the chamber; however, there appears to be some evidence that the observed phenomenon is not necessarily a particular detonation or even a strong shock wave. Although there is no doubt that combustion occurs along the wave front as it rotates around the chamber, there appears to be no positive indication of a discontinuity. The pressure data of Figure 9, although indicating a large rate of pressure rise due to the high frequency with which the wave passes the gauge diaphragm, does not demonstrate the nearly vertical characteristic which would occur with the passage of a discontinuity, particularly if it is noted that the time between peaks of the trace shown in Figure 9 represents a full 360° of wave travel around the chamber. This is further borne out by the map of instantaneous chamber wall pressures shown in Figure 13, indicating the smooth pressure variation which would be observed during ordinary combustion following the wave.

The most significant indication that the observed pattern is that of a relatively smooth combustion wave is, however, the measured wave velocity of approximately 6,800 ft/sec which, for a sound velocity of approximately 3,800 ft/sec in the high-temperature combustion gases, represents almost exactly the tangential acoustic velocity of 1.841 times the speed of sound (1). For comparison, if

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the wave were a full Chapman-Jouget detonation, it would propagate
at a Mach number of the order of 3, or about 10,000 to 12,000 ft/sec,
and experience a stagnation pressure ratio across the wave of over
100 to 1 (2).

Further indications that the observed luminosity pattern
is that of an ordinary "slow combustion" wave is provided by the
velocity map of Figure 13, whose gas velocities upstream and down-
stream of the wave fall clearly within the domain of "slow
combustion" as defined in (2). In view of this evidence, it appears
that the rapidity of combustion, although definitely accelerated
by the pressure wave and its associated temperature rise, does not
approach the speed required for even a "partial detonation."

With respect to the experimental cataloguing of the
characteristics of the tangential mode, one of the most interesting
facets explored by the authors is the effect of increasing chamber
diameter. In addition to the basic justification of their analysis
provided by these data, the fundamental symmetry of the wave pattern
is demonstrated by the counter-rotating fronts observed in the
larger motors. The chief point of interest, however, carries beyond
the scope of the research described by Pickford and Ellis into the
general probem of scaling, particularly with respect to the high-
frequency transverse modes of instability. A logical and extremely
useful consequence of this research would be to observe the effect
of various parameter variations on the type and intensity of the
resulting modes of instability. The authors have indicated some
work along this line by their changes in injector spud alignment and
chamber pressure, as well as chamber diameter. A systematic program
of this type would be of considerable significance in outlining
some of the parameter variations which have been suggested in
various scaling rules (e.g., 3). Some of the information which might
be supplied by such a program, in addition to the direct effects on
transverse-mode instability of parameters such as chamber pressure,
chamber diameter, mixture ratio, orifice spacing, propellant velocity,
impingement characteristics, thrust level, amplitude of "trigger"
burst, etc., would be the general sensitivity of this form of
instability to changes in the basic dimensionless groups,
sensitivity to so-called "linear" and "non-linear" initiations of
instability, and, perhaps, the fundamental question of relating
heat transfer rates to stability behavior.

One final point should be made with regard to the overall
philosophy of the subject paper. Its purpose is clearly to
catalogue and describe as accurately as possible what happens in a
rocket chamber during the existence of a tangential mode of
instability. It is the opinion of this author that Pickford and
Ellis have succeeded admirably in performing this function. However,
it is also the opinion of this author that the fundamental question
which must be answered before this form of instability can be
totally eliminated is not "What is happening?", but rather "Why is

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It happening?". Specifically, the overall answer to combustion
instability problems lies in a complete description of the
mechanism by which natural modes of chamber gas oscillation are
coupled to the combustion process so as to provide reinforcement of
these modes, and, further, the manner in which this coupling is
affected by parameters which can be manipulated by the thrust
chamber designer. Considered in this light, the research described
by Pickford and Ellis has provided considerable enlightenment
concerning the nature of the phenomenon, and has appreciably
shortened the road to eventual elimination of a crucial problem in
rocket motor technology.

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GENERAL DISCUSSION

DR. ZUCROW: I didn't come here prepared to discuss what we were doing in this field at Purdue University. I am of the opinion that we should study these phenomena quite fundamentally, and at Purdue we have been studying what happens with premixed gases. We have compiled a list of variables which may influence combustion pressure oscillations. To study the influence of each one of them separately is going to take a long, long time.

It is true that a lot of time and money has been spent studying combustion pressure oscillations, and that much of the effort is not too fundamental, I will agree. One must realize, however, that institutions which have no responsibility for the delivery of hardware can be very fundamental. The poor chap who has the responsibility of delivering hardware to the Army, Navy, or the Air Force on a time schedule must have pretty quick fixes if he is in trouble and expects to stay in business. I think Dr. Ellis did an extraordinary job in giving us insight into what one can do to get himself out of difficulty. I think he deserves great congratulations from us all in the rocket motor industry.

MR. TORMEY: The next paper involves the subject of regenerative cooling. We have had papers on propellants, propellant performance, instability, combustion instability, throttling action, and heat transfer. This is the first paper which deals with the use of propellants as regenerative coolants.

PAPER

FACTORS WHICH INFLUENCE THE SUITABILITY OF LIQUID PROPELLANTS AS ROCKET MOTOR REGENERATIVE COOLANTS

by D. R. Bartz
Jet Propulsion Laboratory, California Institute of Technology

(See pages 260 to 283, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by W. T. Olson
(Presented by H. C. Barnett)
National Advisory Committee for Aeronautics

Discussion Prepared by
Dr. Walter T. Olson
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Lewis Flight Propulsion Laboratory
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Cleveland, Ohio

on D. R. Bartz Paper
FACTORS WHICH INFLUENCE THE SUITABILITY OF LIQUID
PROPELLANTS AS ROCKET MOTOR REGENERATIVE COOLANTS

Mr. Bartz in his very excellent paper has stated that his ob-
jective is to present and to discuss the factors which determine the
suitability of a given propellant as the coolant for a completely re-
generatively cooled motor. As he has pointed out, it is practically
impossible to calculate a physical property that will characterize the
potentialities of a particular propellant as a coolant relative to
other propellants. Consequently, he has very wisely chosen to illus-
trate the margin that may exist between the upper limit of nucleate
boiling and the heat transfer rate that might occur at the throat of
a rocket engine. Any review or criticism of Mr. Bartz' work is more
liable to be embellishment than correction.

As an embellishment, then, heat transfer at supercritical condi-
tions might be discussed in a bit more detail than the author has
done. Supercritical heat transfer of course occurs when the coolant
is above its critical pressure. Heat transfer under these conditions
is most liable to be encountered with the high energy propellants that
lie beyond the current jet fuel liquid oxygen combination in terms of
performance. And here we are concerned with only a limited number of
propellants. My subsequent remarks will bear largely on high energy
propellants.

Jet fuel - liquid oxygen with a combustion temperature of 5500°
to 6000° F has been demonstrated to cool adequately in thrust chambers
up to as large as 150,000 pounds. Beyond this combination in per-
formance are mixtures of fluorine and liquid oxygen with jet fuel.
Here too, fuel cooling has been demonstrated - at least to 15 percent
fluorine addition.

The highest performing stable chemical combination is hydrogen-
fluorine. Its maximum specific impulse is at about 18 percent

hydrogen in the combination. Attendant combustion temperature is about 5000° F. The bulk density of this propellant combination can be more than doubled by running the mixture at about 5 percent hydrogen. In this case more than 8500° F is encountered in the combustion chamber. While prospects look encouraging for cooling with 18 percent hydrogen, they begin to look dubious for 5 percent hydrogen. One would want to shift toward the lower hydrogen concentration to improve on the tank volumes and pump sizes required for hydrogen. The inevitable engineering compromise will occur among missile volume and empty weight, engine specific impulse, and engine cooling.

Another high performing combination is hydrogen - oxygen. Here combustion temperatures for maximum specific impulse are of the order of 4500° F, while improving the bulk density puts temperatures up to over 5800° F. In some early experiments with the combination, hydrogen was used as the coolant.

Still another combination is ammonia with fluorine, or mixtures of ammonia and hydrazine or even just hydrazine with fluorine. Combustion temperatures here are in the 7000° to 8000° range. Some experiments with ammonia-fluorine have burned out experimental engines.

A big question of course is: Can these combinations regeneratively cool? Figure 1 shows the heat flux per unit area obtainable as a function of wall temperature for several of the propellants that I just mentioned, with the calculations having been done for fluid velocities that give reasonable pressure drops. As Bartz has already shown, ammonia cools quite well up to the nucleate boiling range, at which point the expected dramatic drop in heat transfer coefficient reduces the heat flux by a factor of 20. Liquid oxygen and like it, liquid fluorine, as well as methane show modest cooling. Hydrogen, although operating as a gas or as a single fluid, that is supercritically, shows cooling capabilities as good as or in excess of those obtainable with nucleate boiling. As long as the combustion temperatures with hydrogen combinations are not grossly in excess of those that are now being cooled with jet fuel the prospects for cooling look quite good. With the combination of limited cooling capability and high combustion temperatures for ammonia or hydrazine or their mixtures with fluorine, cooling looks exceedingly difficult.

This much discussion brings up a point that Bartz has raised in his paper. He has pointed out the need for values of transport properties, particularly viscosity and thermal conductivity. Admittedly measurement of these properties, particularly thermal conductivity, is difficult at the temperatures that we are discussing, and the data in the literature are skimpy. However, there are data for the reasonably finite number of propellants that are of interest. Further, although these data do not specifically cover the range of operating conditions of interest they can be used for engineering design purposes with extrapolation. After all, local aberrations in

wall smoothness or in wall thickness, or errant streams from rocket injectors can produce far more drastic effects on cooling than 25 to 50 percent variations in a computed heat transfer rate. What is more important, as long as there are such severe limitations on our knowledge of how to achieve the upper limit of heat flux with nucleate boiling it would be better to design as close to the lower limit of heat flux for nucleate boiling as possible, and use our nucleate boiling as a safety factor to the extent possible. I'm sure that this is not an uncommon practice actually.

With that I would like to go out on a limb and say that data sufficiently adequate for the needs of the hour exist. Specifically, some data on transport properties exist for ammonia, typical hydrocarbon fuels, hydrazine (l), hydrogen, fluorine (g), and oxygen provided some extrapolation is accepted. Data virtually absent include thermal conductivities for chlorine trifluoride, hydrazine (g), fluorine (l), and u-dimethylhydrazine. Viscosity data are missing for hydrazine (g) and u-dimethylhydrazine (g). But may not hydrazine explode above 400° F anyway?

Also, regarding the use of transport properties, consider figure 2. Part (a) of the figure gives the Seider-Tate equation for heat transfer coefficient. Now the viscosity and the thermal conductivity appear in here as a ratio, and this ratio is relatively insensitive to temperature and pressure since temperature and pressure affect each of these terms rather similarly. Further, where viscosity appears alone it appears to a low power. Had Nusselt number been used for this heat transfer relation instead of Stanton number, errors in heat transfer coefficient would depend directly on thermal conductivity. An additional advantage of this equation is that Stanton number can be evaluated from experimental data directly with no physical properties being involved. Note that in this form all of the properties are evaluated at the bulk temperature except viscosity, and a ratio of correction for viscosity at the wall is used; however, here it is to a low power. It should be less difficult to find properties at the lower, bulk temperatures than at the film temperature.

Part (b) of the figure expresses the heat transfer coefficient with fluid properties included at their values at the effective film temperature. This expression is a better representation of experiment when large differences between wall temperatures and fluid bulk temperature exist than is the equation in figure 2(a). Unfortunately, this large temperature difference is encountered in rocket cooling. As a result, both bulk and film density must be used, and the other properties must be evaluated at higher-than-bulk temperatures. This expression (fig. 2(b)) was used for the curves of figure 1. Other methods of evaluating heat transfer coefficients for high temperature gradients and high flux rates are under study.

CONFIDENTIAL

I hope that I am not construed as having come out against the measurement of more physical properties for fluids. Indeed we need these. A particular time when the engineering becomes difficult is when pressure drop changes or surges with nucleate boiling or with cavitation. However, my point is that we can do much of our engineering with what is already at hand.

Some further comments may be made on the paper. The first of these is that the criterion of using the combustion side wall temperature for no failures as Bartz has done requires a calculation of this wall temperature. Now that is quite often far the more difficult part of the heat transfer problem. Complications such as transport of enthalpy through the boundary layer by dissociated species are added. Now, too, the lack of transport properties is more serious.

Bartz has mentioned that perhaps more than one method of cooling could be used at the same time. Where that can be done it is certainly to be recommended. For example, why should we not always try to have a coating on the inside wall of a rocket? Continuously formed coatings, for example, the carbon coatings that result from rich combustion of jet fuel have been shown to reduce heat transfer rates. Perhaps such coatings, or permanently bonded ceramic coatings, could always be used. Still another thought is that turbulence could be introduced in a particular way at critical points inside the coolant passages to increase local heat flux rates.

In the written version that I reviewed the second paragraph of the conclusions is a bit confusing in its wording. It is presumed here that the author means to state that sufficient coolant flow should be provided so that local heat flux from the combustion gases to the wall, and therefore from the wall to the coolant, do not exceed the upper limit of nucleate boiling at any local point.

CONFIDENTIAL

CONSTANT PRESSURE HEAT ABSORPTION
RATES FOR SEVERAL COOLANTS

Figure 1

HEAT TRANSFER COEFFICIENT
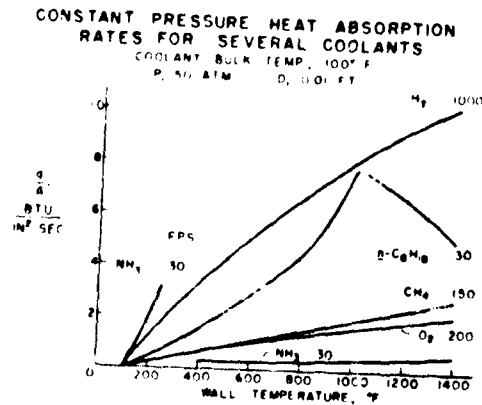
(a) PROPERTIES AT BULK TEMPERATURE, EXCEPT μ_w

$$h = 0.023\ C_p \rho V \left(\frac{C_p \mu}{k}\right)^{-0.67} \left(\frac{D \rho V}{\mu}\right)^{-0.2} \left(\frac{\mu_w}{\mu}\right)^{-0.14}$$

(b) PROPERTIES AT $T_f = \dfrac{T_{bulk} + T_{wall}}{2}$

$$h = 0.023\ C_{p,f} \rho_f V \left(\frac{C_{p,f} \mu_f}{k_f}\right)^{-0.6} \left(\frac{D \rho_f V}{\mu_f}\right)^{-0.2}$$

Figure 2

GENERAL DISCUSSION

MR. BARTZ: I would like to reply to a couple of points in Dr. Olson's extensive comment.

First, I do not believe that limiting the design of regeneratively cooled systems to the lower limit of nucleate boiling is at all necessary. For many coolants, operating at pressures up to about 70% of critical pressure, the ratio of the heat flux at the upper limit of nucleate boiling to the heat flux at the inception of nucleate boiling is between about three and ten. To suggest that safety factors this large should be used in the design of regeneratively cooled ⋯⋯⋯ would indicate little or no faith in analytical methods ⋯⋯⋯able for predicting heat flux to the motor walls from the ⋯⋯tion gases. In my opinion these analytical methods, together ⋯⋯ prototype development testing, should permit design with consid⋯⋯⋯y lower safety factors, such that nucleate boiling heat tran⋯⋯r can and should be used. We have found that q_{ul} data, measure⋯ with coolants having well-controlled composition, have been reproducible to within 10%, so that for such systems perhaps a reasonable design limit would be 70% or 80% of reported q_{ul} values.

Dr. Olson comments that calculation of wall temperature is difficult and uncertain and thus a bad criterion for determining whether or not the cooling is adequate. If the conditions in the cooling passage are such that heat is being transferred by nucleate boiling, it is pointed out in the paper that the wall temperature on the coolant side is easily predicted to within 50°F knowing only the saturation temperature of the coolant. Thus, the difficulty comes in calculating the drop through the wall. For a thick wall, I would tend to agree with Dr. Olson that prediction of gas-side wall temperature is difficult and uncertain, since the accuracy of the prediction depends directly upon the prediction of local values of heat flux to the wall. However, for the extremely thin walls currently used in most flight-weight motors, the temperature drop through the wall is small, and thus its accurate prediction is not important in predicting gas-side wall temperatures. For such motors, if the saturation temperature of the coolant is below about 700°F, cooling is adequate if moderate boiling is maintained. However, in the final analysis, irrespective of the difficulty of prediction, the success or failure of the cooling design depends on the resulting combination of local wall temperature and stress.

I certainly agree with Dr. Olson that refractory coatings should be utilized to the limit of their capabilities as barriers to heat transfer in rocket motors. I might point out that such coatings, which are currently good to about 3000°F, can reduce heat fluxes by over 50% for systems operating at flame temperatures in the region of 5000°F. However, for a high-energy system operating near 8000°F flame temperature, the reduction in heat flux effected by such a coating would be less than 30%. Hence, while the use of refractory coatings will help,

regenerative cooling will also have to be used to the limit of its capability to successfully cool the high-energy systems of the future.

Finally, I would like to allay Dr. Olson's fears that cooling with hydrazine is not possible or feasible. We have initiated heated tube measurements with hydrazine since the writing of this paper, and we are finding hydrazine a better coolant than any of those propellants listed in Table 1 of the paper, second only to water. These measurements are being reported in the Combined Bimonthly Summaries of the Jet Propulsion Laboratory starting with Number 57 for the period of December 1956 to February 1957. The anticipated difficulty with the use of hydrazine as a coolant, thermal decomposition, can be avoided by using compatible materials of construction (e.g., 18-8 S.S. or aluminum alloys) and by designing the co system to be free of stagnant regions where the hydrazine migh . A series of 63 tests in which a motor was successly with hydrazine as a regenerative coolant was reported by io in Jet Propulsion Laboratory Progress Report No. 20-156, d December 4, 1951.

PAPER

FACTORS INFLUENCING THE MONOPROPELLANT
SPECIFIC IMPULSE OF ACETYLENIC COMPOUNDS

by Lloyd E. Line, Jr.
Experiment Incorporated

(See pages 284 to 298, Volume 1, JFL 212/13)

PREPARED DISCUSSION

by Seba Eldridge
Aerojet-General Corporation

(See following pages, 93 to 94)

CONFIDENTIAL

Discussion Prepared by
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on Lloyd E. Line, Jr. Paper
FACTORS INFLUENCING THE MONOPROPT SPECIFIC
IMPULSE OF ACETYLENIC COUNDS

Discrepancies between the theoretical and experimental performance of acetylenic monofuels have been widely observed. Certainly a better understanding of the nature of these differences is required if maximum use is to be made of this interesting group of monofuels. Mr. Line has made a significant extension of Dr. Glassman's earlier work in this area.

A review of Mr. Line's paper makes it clear that, although certain possibilities have been eliminated, a complete understanding of the nature of the decomposition and subsequent flow processes is not yet at hand for the acetylenics. Both Mr. Line's paper and some experimental work performed at Aerojet have suggested further avenues for investigation of this problem.

Extensive tests conducted with iso-propylacetylene (IPA) over quite a range of operation conditions have indicated that:

1. The experimental value of the "characteristic velocity," c^*, is appreciably lower than the theoretical value; and,

2. The measured flame temperature is only slightly lower than the theoretical value.

The combination of these two factors provides an aid to the examination of various possible explanations for observed "low" performance. First of all, it should be pointed out that the parameter c^* is really the inverse of the gas volume production by a given reactor. This parameter is, of course, directly related to the specific impulse by the relationship $I_{sp} = C_f c^*$, where I_{sp} is the specific impulse and C_f the nozzle thrust coefficient. The thrust coefficient is not significantly influenced by the reaction process; therefore, the parameter c^* can be referred to for an indication of what happens upstream of

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the nozzle. The two experimental facts cited above lead us, therefore, to seek a mechanism for observed "low" performance which will result in relatively low gas production rates but normal flame temperatures.

The consideration just cited leads one to reject some of the mechanisms suggested by Mr. Line. As he has pointed out, the formation of methane would lead to higher flame temperatures as well as reduced performance, and these higher flame temperatures have not been observed in the decomposition of IPA. Similarly, the presence of most of the hydrocarbons in the gas phase reduces gas volume per unit weight flow and hence performance; but such compounds increase flame temperature. This is not true of a few of the ring compounds such as benzene. The presence of benzene would reduce both the flame temperature. The simultaneous presence of, say, methane and benzene might then yield values of performance and flame temperature agreeing with the experimental results. This mechanism has been suggested by Messrs. Greene and Gordon of our organization; we are hopeful that experiments planned for the near future will allow us to confirm this hypothesis.

As Mr. Line has recommended, experimental studies of the kinetic mechanisms occurring in the decomposition of acetylenic compounds are very much needed. It can be expected that such studies will allow us to tailor gas reactors to more nearly obtain the performance desired. Certainly all available evidence points to the fact that chemical rather than mechanical processes govern these reactions; hence, it should be possible to control the reaction by techniques applied upstream of the nozzle.

CONFIDENTIAL

GENERAL DISCUSSION

MR. LINE: Mr. Eldridge has referred to the fact that the measured flame temperature is very near the theoretical temperature although the concentration of the methane seems to be quite high.

As an alternative to his explanation of benzene or benzene-type compounds as heat sinks, I would offer another explanation. In my presentation, I showed that the enthalpy content of the carbon is considerably higher than that of graphite so that carbon may be responsible for absorbing heat and maintaining the tem̄ ̄ure at about the theoretical level. I have no calculations o̅ ̄ , however.

I. GLASSMAN (Princeton Univer̄ ̄. I wish to comment on Mr. Line's paper, as I warned him ear̄ ̄ .

First of all, I am glad ̄ ̄ see that three or four organizations -- Aerojet, Experiment Inc̄porated, and Princeton -- are gradually obtaining an understanding of the problem of low performance in acetylenic compounds. I would like to offer one comment that perhaps the reasons for the low performance may not be tied up to many errors but to one large error we have been overlooking.

I have two suggestions to make. In regard to the comments about methane, as mentioned in the Line paper, he obtained abō a 30% methane. In some work we had done previously we measur̄ ̄ ̄ethane. Nevertheless, I don't think this will answer the problem. The differences in sampling in rocket motors are enormous and I dōut whether any of the values are really exact or really will answer this particular problem. Prior to hearing Mr. Eldridge's comments I intended to offer a new idea which I hope will assist in answering all of the low performance problems with acetylenic monopropellants. The comment that Eldridge made, I feel, supports the new idea I propose.

Mr. Eldridge pointed out that the temperature which Aerojet measured with isopropenyl acetylene was near theoretical but the C* measurement was not. This result could only be explained on the basis that the correct ratio of specific heats was not used. Then it appears that the performance problem arises not from a chemical factor, but from a physical factor which affects the average ratio of the specific heats. That this possibility can arise I wish to explain as follows:

I think we have overlooked the fact that these solid carbon particles which are present in the exhaust of an acetylenic decomposition process can absorb gases physically or chemically. It is not beyond comprehension to think that a monomolecular adsorption of hydrogen could take place in the chamber and as the carbon particles are exhausted from the rocket the hydrogen is retained on the particles. These particles would stay physically adsorbed. I think the calculation to verify this postulation would be simply as follows. One can determine the collision diameter of the hydrogen at the proper

temperature. Knowing the surface area of the particle from the particle size determinations carried out by Experiment Incorporated and Princeton, one can tell how much hydrogen would be adsorbed in a monolayer. We have so much carbon present that it is feasible that a large volume could be adsorbed in this particular case. I think it is one factor no one has looked into as yet. I think it is something that is worthwhile considering and calculating.

I also wish to point out that in the work done in England with the acetylenic compounds performances closer to 100% were obtained. While I realize that there were, I believe, just a few results, it would be interesting to pursue this point further with the British.

One other fact I would li... , point out in dealing with rocket motors in these hybrid p~ ...nts, even though you do lose performance in the actual rocket ... all the performance disappears. It would be nice to have it ... in the thrust of the rocket and in the afterburning, but some of the results of our ram rocket work show that you do pick up this particular loss of energy later in the afterburning process.

MR. LINE: I wish to thank Dr. Glassman for warning me about his comments because in the meantime I have had a chance to make the calculation which he proposes.

Of course, these particles are of the order of 10^{-5} centimeters or 1000 Ångstrom in diameter. If you put ... this 1000 Ångstrom particle a monolayer of hydrogen (as proposed), it turns out that, unless my calculation is wrong, the percentage of the hydrogen is of the order of .02. (The ratio of the hydrogen to carbon is about .02.) This is much less than that found experimentally. It is therefore difficult for me to see how monolayer adsorption can be a serious factor.

With regard to the recovery of the loss in the monopropellant decomposition part of a ram rocket, of course, it is true that you will thermodynamically recover this in terms of enthalpy. On the other hand, we know from thermodynamics that you can get a higher cycle efficiency when you operate at higher pressures, so that in the ram rocket stage you are better off by having as high a specific impulse as possible. Furthermore, for some applications it is important to have as high a monopropellant efficiency as possible.

Comments Submitted After the Symposium
by John Happel
New York University

I would like to add a little supplementary information regarding the kinetics of decomposition of acetylenic materials. We had a program at New York University for the generation of hydrogen, which was under contract with the Army Signal Corps for several years. In this connection we studied the adiabatic self-sustained decomposition of a number of the acetylenic compounds listed in Table II of Mr. Line's paper. We confirmed the presence of substantial portions of methane, as indicated by Mr. Line. We also found that some of these compounds decomposed much more rapidly than others, thus methylvinylacetylene decomposes faster than methylacetylene. We also found that the rate of decomposition could be accelerated by the addition of small amounts of additives, such as ethylene oxide. It may be that the primary rate of decomposition, rather than later reaction to decompose methane formed, may have a bearing on the lower performance observed with some of the acetylenic materials which have been tested in actual rockets.

For informational purposes it might also be mentioned that the compounds which we tested were essentially the same ones as noted in Table II. Since these compounds were furnished to Experiment Incorporated by the New York University laboratories there should be no essential differences due to slight traces of undetermined components. This information might also be of interest to those desiring to do further work on the synthesis or properties of these materials.

PAPER

EFFECT OF HYPERGOLICITY OF THE PROPELLANTS ON THE OPERATION OF A LARGE MISSILE ROCKET

by R. F. Pangren
(Presented by Mr. Nathaniel Van de Verg)
Aerojet-General Corporation
(See pages 299 to 304, volume 1, F 212/13)

PREPARED DISCUSSION

by Stanley Greenfield
Rocketdyne

(See following pages, 99 to 101)

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Discussion Prepared by
Stanley Greenfield
Rocketdyne
Canoga Park, California

on R. F. Tangren Paper
EFFECT OF HYPERGOLICITY OF THE PROPELLANTS
ON THE OPERATION OF A LARGE MISSILE ROCKET

Apparently the main reason for changing the BOMARC fuel from JP to JPX was to avoid the destructive low frequency vibration caused by the combination of the combustion lag of the propellant combination and the thrust chamber geometry, the resonant frequency of the feed system, and the hydraulic and/or mechanical coupling between the thrust chamber combustion and the propellant feed system.

Essentially, this low frequency vibration could have been reduced or eliminated by making the propellant feed system less dependent on the combustion processes, that is by dynamic decoupling. This decoupling in turn could have been accomplished by changing the natural frequency of the supply system, by altering the retarded transfer function (that is, the fidelity with which a change in flow rate is reproduced in the chamber pressure, and the phase relationship between the two) so as to make the "combustion time lag" significantly different from half the natural period of the supply system, or by increasing the dynamic damping.

In the BOMARC system, the resonant frequencies of the system could have been altered by changing the mechanical stiffness or by modifying the hydraulic length of the feed system or the head differential between the tank and the chamber. However, these methods would all have required hardware modifications, and still might not have altered the resonant frequencies sufficiently.

The feed system impedance could have been changed by raising the injector pressure drop or increasing the frictional losses in the system, or even by adding an energy accumulator. Again, hardware modifications would have been necessary.

The introduction into the injector manifolds of a vibration of opposite phase from the induced vibration would have been theoretically possible, but practically very difficult.

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The best solution would appear to have been a significant change in the character of the "combustion time lag," for in this case any later modifications to the feed system would not have been likely to bring about close coupling again, due to slight changes in the feed system resonant frequencies. An injection pattern with improved mixing and atomization would have decreased the combustion time delay, and this might have reduced the amplitude of the vibration by allowing less propellant accumulation per cycle but possibly could have led to some of the high frequency vibrational troubles previously encountered with high performance injectors. Operation at off-optimum mixture ratio would also have altered the combustion characteristics, but only at a severe loss in performance.

The solution that Aerojet chose, the use of a hypergolic propellant combination to reduce "combustion lag," also had the advantage of improving the low temperature starting characteristics, and so certainly seems to have been the best choice under the circumstances.

However, hypergolicity by itself is not the only factor determining "combustion time lag" even with a particular injection system and chamber configuration, and so was not necessarily the reason for the success of JPX. Such characteristics as flame speed, volatility, and combustion limits can more than offset advantages due to hypergolicity. As an extreme example, a non-hypergolic combination such as oxygen and hydrogen would probably cause considerably less trouble from low frequency instability initiated through a "combustion time lag" mechanism than would a combination of RFNA and JP with just enough UDMH to make it hypergolic under standard conditions. In the more limited case of the substitution of one element of a non-hypergolic system with a hypergol (with a similar liquid range), the resulting hypergolicity probably gives a good qualitative indication of the combustion time lag.

With liquid oxygen as the oxidizer (as in the case of all the large engines at Rocketdyne), low frequency instability due to combustion time lag is much less of a problem than with acid as the oxidizer. Low frequency instability due to combustion lag, while not encountered during normal operating conditions at rated pressure, has occurred in large engines during starting and throttling, at which time the atomization of the propellants is very poor and the system pressure drops are low.

Due to other than propulsion requirements, throttling during the last few seconds of operation in the 150,000 pound thrust LOX-RPI JUPITER engine has been necessary, and vibration has occurred at about 150 cps and ± 75 psi when the engine was throttled from its rated 500 psi chamber pressure to about 2/3 to 3/4 of rated conditions.

Rocketdyne has about the same set of possible solutions to this problem as had Aerojet, with the same underlying criteria of minimizing the changes in engine configuration without decreasing the overall performance. These conditions eliminate many of the choices.

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For example, changing the flow system to any appreciable extent to alter the impedance is not allowable. The only standard fuel which might reduce the "combustion time lag" without reducing the performance with the existing tank volumes is DETA, and then major pump rework might be required.

The methods of solution to this problem which appear most feasible are:

(1) Eliminate the throttling requirement. Improvements in guidance equipment and controls may increase the allowable acceleration.

(2) Tolerate the vibration, which is not extremely severe and lasts only a short time. This, of course, would be a last ditch stand.

(3) Run at fuel rich mixture ratio conditions during these few seconds and accept the slight performance loss, if the present requirement on propellant flow control can be changed. Experience has shown that the fuel rather than the oxidizer atomization is critical in order to avoid low frequency vibration in a LOX-RP1 system, and this low mixture ratio running will keep the fuel injection pressure drop high and tend to improve atomization.

(4) Several different injector configurations should be tested, one of which may change the low frequency instability characteristics and at the same time not introduce high frequency instability during main stage. Use of an injector, which has a high enough pressure drop to produce fair atomization at low flow rates, tends to introduce high frequency instability during main stage due to the extremely good mixing and atomization under these conditions. High frequency vibration has already been encountered during the steady state with some injection patterns. Unfortunately, there is no proven theoretical basis on which to design injectors to accomplish these results, and still produce good performance, so that it may be necessary to test many different patterns. This approach, however, is the only one over which Rocketdyne has full control, and it is the approach which is being followed at the present time.

GENERAL DISCUSSION

JOHN MARSHALL (Air Force Flight Test Center): The destruct-
ive malfunction of the free flight BOMARC as described by Mr. Tangren,
was not noted in the pre-flight test stand tests. It can be deduced
that the vibrational energy coming from the combustion chamber distri-
butes itself throughout the elastic masses of the free flight missile
in one way, and in another way on the captive missile. The test stand
absorption of the captive flight missile vibrational energy is thus
definitely not negligible, as shown by the BOMARC malfunction.

Do you think that the conventional test stands, like those
that were used for testing the BOMARC, ought to be modified so as not
to distort the low frequency vibration distribution over the missile
during captive flight tests? What has Aerojet done to change the de-
sign of conventional test stands?

MR. VAN DE VERG: We agree with your comments concerning the
important effect of the mounting on the combustion stability of the
rocket engine. Other development programs at Aerojet have included
firing tests in which the propulsion system was held by very soft mounts
in an endeavor to assure that successful flights would follow. The
BOMARC program did include a great deal of dynamic testing in which the
structure was vibrated under a variety of different conditions. I do
not have details concerning these tests here. The point concerning the
importance of dynamic mounting of the rocket engine is well taken and
pertinent tests should be included as a part of every development pro-
gram.

28 MARCH 1957
AFTERNOON SESSION

CHAIRMAN: COMMANDER R. C. TRUAX

DONALD B. BROOKS (OASD - R&E): Our chairman has been detained for a few minutes. Until he arrives, I will substitute for him. To begin the session, Mr. Hornstein will review the papers which have been submitted for publication only.

BERNARD HORNSTEIN (Office of Naval Research): I think Mr. Brooks may have expected some rather astute comments. If this is the case, you will be highly disappointed.

In a situation like this, we receive many more papers than we have time to present and, since man, of the papers do contain information of value and interest, they will be published nonetheless. I would like to indicate the titles and summarize briefly what they are about.

The first is "LIQUID PHASE IGNITION OF ELECTROLYTIC MONO-PROPELLANTS BY ELECTRICAL DISCHARGE," by Eva, Given, and Muller of Stanford Research Institute. This is an elegant piece of work on the detailed structure and process occurring in an electrical discharge submerged in the hydrazine nitrate-hydrazine-water monopropellant system and describes very nicely the nature of the discharge and presents hypotheses about the process of energy transfer to the monopropellant and ignition.

Another paper is "A SURVEY OF LIQUID PROPELLANTS FOR GUNS," by Regan of Frankford Arsenal. This paper describes the status of the development of three liquid propellant gun systems: an aircraft, rapid-fire gun, using pre-loaded hydrazine, hydrazine nitrate water monopropellant and similar ones using liquid injector bipropellant systems; it covers a shoulder weapon, .30 caliber, using propyl nitrate monopropellant systems; and larger caliber tank guns, using both bipropellant and monopropellant systems.

Another paper, "EFFECTS OF CHEMICAL COMPOSITION OF JP-4 FUEL ON LIQUID ROCKET THRUST CHAMBER COMBUSTION CHARACTERISTICS," was reviewed in effect by Mr. Ellis of Aerojet, this morning. A great part

of what was in this paper formed the substance of Mr. Ellis' comments earlier.

Bell Aircraft, Messrs. Potter and Wayman, submitted a paper on the "HYPERGOLIC IGNITION OF LIQUID OXYGEN/HYDROCARBON ROCKET ENGINES." The successful compounds were aluminum alkyls: triethyl aluminum, diethyl aluminum monohydride, and triisobutyl aluminum.

Another paper, submitted by Happel and Marsel, New York University, entitled "ACETYLENIC COMPOUNDS FOR ROCKET FUELS," arrived after the preprints were issued and is not included in Volume 2 of the preprints. This paper presents the properties, stabilities, and calculated performance values for several acetylenic compounds and blends thereof as fuels for ram rocket and turborocket systems.

"SOME ASPECTS OF OXYGEN FLUORIDE AS A ROCKET OXIDIZER" is the title of a paper by Muraca of Jet Propulsion Laboratory. This lists the properties of oxygen fluoride, discusses its suitability as a rocket oxidizer, and makes comparisons with oxygen fluorine mixtures.

A paper entitled "NORMAL PROPYL NITRATE: COMPOSITION OF THE COMMERCIAL MATERIAL AND SOME PHYSICAL PROPERTIES OF THE PURE COMPOUND," was submitted by Beatty of the Ethyl Corporation Research Laboratories. This is a compilation of some data primarily on the very pure material and is a refinement of previous values determined by the Ethyl Laboratories and others. It will be of interest to those concerned with the use of normal propyl nitrate.

Cuddy of Wyandotte Chemicals Corporation has written a paper on "AN ADIABATIC AIR COMPRESSION DROP WEIGHT TESTER FOR LIQUID MONO-PROPELLANTS." This paper describes very nicely the high degree of refinement necessary both in design and technique needed to get reproducible ignition results by a drop weight tester. The paper also includes relative sensitivity values for a number of monopropellants.

Another paper on shock testing by Hannum of Hefco Laboratories is entitled "HAZARD TESTING FOR MECHANICAL IMPACT." This describes rather briefly an apparatus for determining the impact sensitivity for materials at controlled temperatures, including temperatures at which the sample exhibits a high vapor pressure.

A paper I was glad to see was the "TRANSIENT AND STEADY STATE HEAT TRANSFER PROBLEMS ASSOCIATED WITH ROCKETS UTILIZING LIQUID OXYGEN." This is by Lieberman of Edwards Air Force Base. This is a detailed analysis of the sources of boil-off, in an installation for the handling, utilization, transfer, and storage of liquid oxygen and includes analysis of losses in several components of the system, indicating the nature of the losses and the approaches possible to minimize them. It contains rather alarming figures on the proportion of LOX purchased to that which is actually used in a test run.

Mr. Forbes, Wright Air Development Center, has a brief paper on the "STORAGE AND HANDLING OF LIQUEFIED FLUORINE." He describes the development and field testing of a prototype no-loss system for the storage, transportation, and transfer of liquid fluorine.

Also from Wright Air Development Center, by Dr. Harris, is a paper entitled, "A METHOD FOR ELIMINATING THE EFFECTS OF RESIDUAL NITRIC ACID IN ROCKET ENGINES AND RELATED EQUIPMENT." This describes a cleaning system which briefly involves waterwash, treatment with anhydrous ammonia, and treatment with phosphoric-chromic acid solutions. An engine so treated can be stored apparently indefinitely without corrosion or other debilitating effects.

There are two papers on field tests of propellants, one entitled, "FIELD TEST KITS FOR CORPORAL FUEL AND OXIDIZER," in which Muraca Vango, and Taylor of Jet Propulsion Laboratory describe the analytical procedures for the determination of nitrogen dioxide, water, and hydrofluoric acid content of RFNA, and the hydrazine and water in the fuel, which is an aniline furfuryl alcohol and hydrazine mixture. The series of tests indicated are rather precise and rather rapid in execution.

Also reported is, "A FIELD METHOD FOR DETERMINATION OF HYDROGEN FLUORIDE IN FUMING NITRIC ACID," by Forbes of Wright Air Development Center. The determination of HF is based on the current generated by the spontaneous electrolysis of dilute hydrofluoric acid solutions in a cell by platinum and aluminum electrodes.

COMMANDER TRUAX. Thank you very much, Mr. Bornstein. My apologies for being a couple of minutes late.

The next item on the agenda is a motion picture on the development of a LAR rocket. This will be presented by Mr. W. R. Fish of the Naval Ordnance Test Station.

MR. FISH: This film on the 5.0-inch Liquid Propellant Aircraft Rocket (LAR) was made for a more general audience than this. It was not made particularly for liquid propellant meetings of this kind. However, it describes the LAR and places particular emphasis on those aspects that are important to the field handling of liquid propellants and liquid propellant rocket systems. In the LAR program, although we did not take this approach in the beginning, in recent years we have taken the approach that it is impractical to handle liquid propellants on shipboard. Of course, this approach is being taken elsewhere in relation to the handling of liquid propellants ashore. So in our design work we have placed a requirement on ourselves to design a rocket that can be loaded at the assembly plant and stored for long periods of time. This imposes certain requirements upon the propellants which I am sure are quite obvious to you. These requirements will be brought out in the film. This film is not complete in that there are some retakes that have to be inserted and some other corrections to be made. I am showing you today what is known as an answer print.

It is not final, ready for release. I thought that it would be important to show it to you today, so I am taking liberties to show you an unfinished product.

The film "TECHNICAL FILM REPORT ON LAR, A LIQUID PROPELLANT AIRCRAFT ROCKET," was shown.

PAPER

SOME PROPELLANT PROPERTIES THAT INFLUENCE THE
DESIGN OF ROCKET PROPULSION SYSTEMS

by F. N. Watts
Rocketdyne, A Division of North American Aviation, Inc.

(See pages 305 to 344, Volume 1, PFL 212/13)

PREPARED DISCUSSION

None

GENERAL DISCUSSION

None

PAPER

A NON-COKING ETHYLENE OXIDE REACTOR

by Loren C. Smith
Wyandotte Chemicals Corporation

PREPARED DISCUSSION

by Homer B. Wellman and John W. Bjerklie
(Presented by Dr. Wellman)
American Machine and Foundry Company

Discussion Prepared by
Homer B. Wellman and John W. Bjerklie
AMERICAN MACHINE AND FOUNDRY COMPANY
Turbo Division
Pacoima, California
on Loren C. Smith Paper
A NON-COKING ETHYLENE OXIDE REACTOR

I   Introduction:

Mr. Smith must be commended for the excellent work he has done on his ethylene oxide gas generating chamber. Specifically, his chamber is exceptional for its low rate of catalytic carbon deposition due to the cold wall principle of operation. Also, his chamber starting technique is commendable because of the efficiency achieved and because of the small surface area of the glow rod starter. The mechanical design is very neat and simple considering the complication of operation. The chamber exhibits a certain amount of versatility in allowing operation at very low L*, and because the stage starting principle is readily applicable to the design of efficiently starting chamber of any flow rate. The Smith chamber is among the best types available for ultimately achieving very long duration runs.

As a scientific tool for investigating a principle of chamber design, the Smith chamber is beyond reproach, and has been the source of extremely significant knowledge. As a chamber for practical application, another look must be taken. As a chamber illustrating a practical method for use of ethylene oxide monofuel, certain reservations are in order. As a chamber for anti-coking, some constructive suggestions may be made.

II   Evaluation of the Smith Chamber:

It is clear that the Smith cold wall chamber is one of ingenious design which is easily assembled through use of fitted threads and common gasket materials. The reactor offers the following advantages:

(1) Rapid and efficient ignition with minimum heated surface.

(2) Staging of reactors which allows attainment of high flow rates.

(3) Operation at low L* due to enforced recirculation or mixing of hot product gases with preheated incoming fuel by reverse flow.

(4) Elimination of all catalytic carbon formation by use of cold walls.

(5) Possibility of adaptation for thermal decomposition of hydrogen peroxide.

However this type of reactor has certain inherent disadvantages:

For starting:

(1) High wattage requirement in order to shorten arm time.

(2) Elaboration of fuel flow control and glow rod power control for starting.

(3) Long delay before full flow is obtained.

For operating control:

Since the Smith reactor cannot be controlled by interrupted flow because of danger of flameout and/or combustion instability, control must be by other means. However, these systems have definite deficiencies as follows:

(1) Suitability of fuel throttling is limited at low reactor pressure by carbon formation, decrease in reaction rate, and impaired recirculation.

(2) Suitability of exhaust throttling is limited at high L* settings both by carbon formation and impaired recirculation.

(3) Use of exhaust dumping for control is not efficient.

For reliability:

(1) Accidental interruption of flow can cause flameout.

(2) A new problem appears to be introduced by the use of regenerative cooling, namely polymerization and the blockage of fuel passages.

These disadvantages are explained below.

III.   Basis of Evaluation:

Any solution to the coking problem associated with ethylene oxide gas generators must be viewed together with other chamber problems. Generally speaking, the most severe problems are starting, control, and coking - the order of importance depending upon the mission to be accomplished.

Utility in starting has been demanded in most practical applications. For this, use should be made of readily available sources of power. Elaborate timing devices or sequencing devices should be avoided, and full chamber pressure should be available as rapidly as possible after turning on the fuel. For electric glow-coil-started chambers, a timed arm period is probably the least complicated starting system since only one operation is required before the actual chamber starting operation. The fastest method for such starting is to use very high wattage; and the most efficient method is programming, and the most utilitarian is to use low arming power. Actual system requirements will ultimately determine the best initiation method for a given application.

Minimum surface area of the glow rod must be a consideration for any chamber in which carbon deposition is a major factor.

The widest range of chamber power output for a given volume chamber can be achieved with the bang-bang system, the hot gas dump valve, or the variable area exhaust nozzle. However, the high L*'s associated with some phases of operation with the latter system can magnify the coking problem. The output range (chamber pressure range) for a given chamber with the high frequency bang-bang (dither) system and fuel flow throttling control increases with L*, but there is evidence that at low pressures the coking problem is aggravated.

Complete freedom of choice of usable control systems for an ethylene oxide chamber can best be achieved by including large amounts of hot material within the combustion zone. This prevents the usual instability or flameout of chambers associated with bang-bang control when the walls cool slightly at part load operation. Needless to say, such a gas generator promotes coke formation and chemical means of carbon prevention are required. Also, chemical means can be used to extend the usable range of chamber pressure for a given L* chamber.

An important consideration for the coking problem with any ethylene oxide decomposition chamber is the use of chemical additives in the fuel and special metallic surfaces in the combustion zone. Also, for chambers having special control systems the principles of fluid dynamics for minimizing carbon deposition is an important consideration. These considerations are in addition to that found by

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Smith, namely, the use of cooled walls for gas generators to prevent catalytic carbon. It might be noted here that the Smith chamber probably depends in part upon its internal fluid dynamics for some of its good anti-coking tendencies.

In the body of his paper Mr. Smith describes a problem with rapid polymerization of ethylene oxide within the regenerative cooling section and around the igniter rod of the gas generator. Polymerization in the fuel passages was shown to be detrimental to long duration operation. His hope for contraversion of polymerization are based on observations of a shift in the regions where polymerization occurs. However, this also raises questions as to the fate of dissolved polymers normally contained in ethylene oxide fuel. There is little doubt that the best solution to both problems in the cold wall reactor would be the discovery of a satisfactory inhibitor which would not only maintain low polymer content during fuel storage, but also retard polymerization in the regions where it is encountered. However, with hot wall reactors, no polymerization problem is encountered because substantial concentrations of high molecular weight polymer are gasified without coke formation. In fact, in our work, we have added substantial amounts of polymer (9000 MW) without seriously impairing reactor operation.

IV.   Reliable Operation with Hot Wall Chambers

Because of the great general versatility achievable with hot wall reactors, we feel that some recent gains on the coke problem associated with such reactors should be mentioned. We would like to discuss the chemical approach and the fluid dynamic approach to prevention of carbon deposition.

Under Air Force Contract AF 33(616)-3170 with Wright Air Development Center, the Research Department of the American Machine and Foundry Company has undertaken the study of anti-coking in hot gas generators. This work began November 8, 1955 and four quarterly reports have been submitted, the latest covering the period ending November 1, 1956. This work is still continuing through 1957, but largely directed toward improved starting characteristics of ethylene oxide.

Our investigations to date have given information which is summarized in Figure 0 showing nine rules leading toward coke-free operation of hot wall generators.

ANTI-COKING SURFACES

With the 1954 model gas generator shown in Figure 1, scores of five hour tests have been completed at coking levels below 10 ppm. As long ago as the second monopropellant conference in November, 1955, Mr. Richard Kirkup of Walter Kidde and Company reported twenty-four hours of consecutive tests of the Navaho reactor in which only ten

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grams of coke was deposited from two and one-half tons of ethylene
oxide fuel containing additive. This corresponds to 6 ppm (six parts
by weight of coke per million parts of ethylene oxide feed). We
have always considered the necessary goal for coke formation to be
zero. In accordance with Walter Kidde's findings, aluminized stain-
less steel surfaces require very little pre-treatment with sulfur
compounds for complete passivation. Likewise our use of a silver
liner merely protects the gases from contact with untreated stain-
less steel surfaces of the reactor walls. More important in the 1954
model reactor, the silver liner serves to conduct heat from the ex-
haust end toward the fuel inlet end of this "straight through"
reactor, and in no way catalyzes the reactions, as was first supposed.
Furthermore, we have found it possible to completely passivate the
stainless steel to attain the same low coking levels reached with
aluminized stainless steel and silver liner. Purely for convenience
we have been passivating the 1954 model reactors by actual running
after cleaning and reassembly. Thirteen of these reactors were used
in our tests, and many of the reactors cleaned and reused for several
series of coking tests. Upon reuse, the reactor is very much easier
to passivate but a newly constructed reactor requires about two
hours of running with 1% sulfur additive and 3% dioxane, and 0.094
inch nozzle instead of the normal .032" nozzle to minimize total
carbon accumulated. Any carbon accumulated has no effect whatsoever
on further accumulations in contradiction to the suggestion given as
one of the possible mechanisms of coke formation. The best passiva-
tion treatment is one or two hours of heating in an electric furnace
at 1500° to 2000°F while passing diluted hydrogen sulfide gas through
the reactor. The exact technique is now being established by us.

USE OF ANTI-COKING ADDITIVE

Of all the sulfur additives shown in Figure 2, disulfide and
dimethyl sulfoxide have been proven to contribute more than 10 ppm
coke formation in the gas phase, however, with each of the other
sulfur additives tried, it has been possible at times to obtain one
or several one-half hour tests in succession with no measurable coke
formation whatsoever. These null results are not due either to in-
accuracies in weighing the gas generator nor to fortuitous loss of
carbon deposit out the exhaust nozzle. Until recently when expedition
of work required multiplicity of tests with the same chamber, no
losses in weight were ever observed in any of the tests. Such losses
are observed in reactors only when about five grams of carbon has
accumulated. It is very important to know that for clean up opera-
tion there is a lower limit of approximately 0.1% available sulfur
required to maintain passivation of the stainless steel surfaces
within the generator. We have also found that a maximum of approxi-
mately 1% of available sulfur is all that can be tolerated without
both transforming the chemistry of decomposition of ethylene oxide
and actually causing coke formation in the gas phase. At 60°F inlet
fuel temperature 3% of thioxane in ethylene oxide gives clean opera-
tion of the gas generator, whereas 6% will not only cause "chugging",

but also severe coking. Moreover, 6% of thioxane will allow severe coking and slightly excessive flame temperature at 160°F inlet fuel temperature.

USE OF COOLANT ADDITIVE

It was early found that the flame temperature in the gas generator must not exceed 1792°F or coke formation in the gas phase ensues with consequent gradual blockage of the exhaust nozzle. It was found that the use of 1,4-dioxane in accord with the calculated amount shown in Figure 3 enables coke-free (below 10ppm) operation up to the highest fuel temperature tested, namely 250°F. A deficiency of dioxane addition,as little as 1.5%,was also proven to cause coke formation in the gas phase.

USE OF IGNITION PRIMER

It is apparent that addition of dioxane necessarily interferes with cold starting of gas generators in a manner which is clearly shown in Figure 4. Our present problem is to suitably lower the ignition temperature of ethylene oxide by the use of another compatible additive, possibly nitromethane which serves as an oxidizer since the sulfur compounds required for anti-coking are easily ignitable. The problem is perhaps confined to determining the optimum concentrations and the right combination of these two types of additives. The illustration of the effectiveness of one combination is given in Figure 5 which shows the temperature rise of the ignitor with time and seconds. A drop of 300°F in minimum temperature required for ignition was obtained with total additive content of 10%. This mixture was unsatisfactory from the standpoint of coking. However, since we have found coke-free operation with as much as 3% 1-thio-4-oxane or thioxane, it is highly probable that we shall obtain the desired results with further addition of nitromethane and 1,4-dioxane in proper proportions.

EFFECT OF L* AND REACTOR PRESSURE

Our 1954 model gas generator was used for all the anti-coking tests only because this proved to be the most economical method of determining the critical factors in coke formation and deposition. It was admitted earlier that in numerous one-half hour tests actually no carbon was deposited but this result was neither predictable nor reproducible at will. We believe that this is due to the critical and variable nature of the internal fluid dynamics in any ("straight-through") gas generator. However, the use of this type of reactor showed the highly critical limitations of L* and reactor pressure ordinarily maintained at 2050 inches and 500 psig respectively. Reduction of L* to 1600 permitted use of 3% less dioxane coolant in the ethylene oxide monofuel. Increase in L* to 2600 caused severe coking throughout the gas phase with consequent plugging of the exhaust nozzle. With hot wall reactors we have been using on-off fuel control.

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In our reports it was also shown that three cycles per second interrupted flow or 'diddling' with 50% fuel on time allowed clean operation at higher fuel temperatures where coolant additive would otherwise have been required. The use of "dithe ing", high frequency cycling (10-30 cps) interrupted flow, for varying the fuel flow lowers the average reactive pressure which tends to aggravate formation. The additive requirements to neutralize this affect have not yet been evaluated. However, the data accumulated to date are sufficient to lend reasonable hope that completely coke-free operation for indefinite periods is obtainable at all ambient temperatures up to 250 or more, and with satisfactory ignitability at all temperatures down to minus 70°F. At this stage of the investigation it appears most important that we develop a reactor of the vortex type so that coke free operation can be achieved by combining the fluid dynamic effect with the chemical methods of coke suppression.

VORTEX CHAMBER

The vortex type chamber is a typical chamber having controlled fluid dynamics. A schematic of this chamber is shown in Figure 6. The fuel enters tangentially, flows along the wall in the liquid or vapor phase and decomposes as it flows spirally toward the exhaust port. Sustained operation is achieved by virtue of the entraining effect of the fuel spray. The relatively high local velocities at the walls, the probable high local turbulence levels, and the lack of any obstructions which could induce stagnation regions should drastically reduce carbon deposition. It is also worthy of note that such a chamber is virtually a two dimensional analogue of the half of the Smith chamber, defined by a dividing line running axially through the injector and glow rod.

Proper design should assure reasonably fast and reasonably efficient electrical starts. Pyrotechnic or bi-propellant starting should also be reasonably efficient. Control of such a chamber is probably initially limited to the use of fuel throttling, exhaust throttling, or hot gas dump valve. However, the bang-bang type of control may be possible if large mass liners of high heat conductivity metal are used throughout. Carbon deposition in such a chamber even with no fuel additive or special surfaces should be of acceptably low values for a large variety of applications. Exceptional anti-coking performance should be demonstrable with such aids as special additives and surfaces.

V   Conclusions:

In conclusion it would appear that the general solution to the ethylene oxide gas generator carbon deposition problem requires a chemical approach in addition to others. The fact that such a solution is nearly at hand is fortunate. Coke prevention by such a means allows the use of hot wall chambers which have high adaptability to various starting and control systems. For special chambers,

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control of the fluid dynamics of the chamber can be extremely bene-
ficial for prevention of carbon deposition. The Smith chamber pre-
sents another very good specific solution to the catalytic coking
problem with its principle of wall cooling. The three methods are
not mutually exclusive, and if, wherever possible, they are all used
together, the carbon deposition problem for ethylene oxide gas gen-
erator chambers should be virtually eliminated. The use of chemical
additives can, and has, greatly relieved the starting problem with
ethylene oxide and extended the low pressure limits of operation with
a given chamber. The Smith chamber has been a superb research tool
for experimental evaluation of starting techniques and prevention of
catalytic carbon.

RULES FOR SUCCESSFUL OPERATION WITH ETHYLENE OXIDE

1. Maintain water content below 300 ppm level in the fuel.

2. Passivate all interior generator surfaces.

3. Maintain passivation by use of a proven anti-coking additive.

4. Control flame temperature below 1750°F with coolant additives.

5. Use a compatible oxidizer to lower ignition temperature.

6. Operate at lowest possible L*.

7. Operate at high chamber pressure.

8. Control flow by on-off interruption.

9. Use controlled fluid dynamics in reactor design to avoid dead spaces.

Figure 0

Wellman & Bjerklie

GAS GENERATOR A.M.F. MODEL -171 (1954)
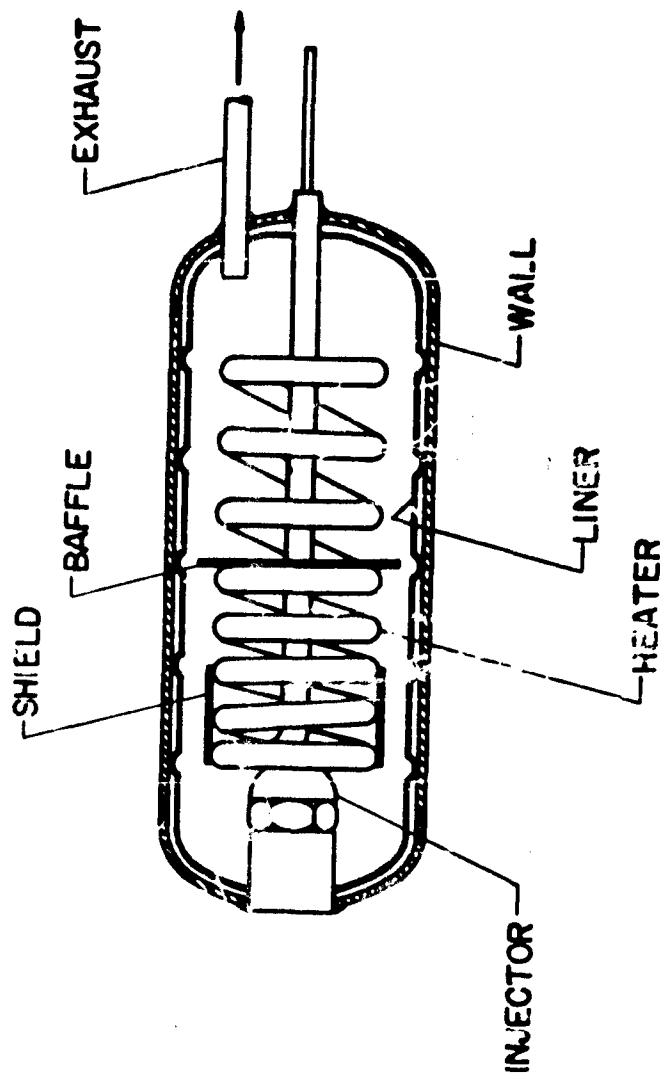
FIG. 1

PROPERTIES OF ANTI-COKING ADDITIVES

	Sulfur content Wt. %	Density g/ml at 68°F	Freezing Point °F	Boiling Point °F
*Carbon disulfide	84	1.263	-163	115
*Methyl sulfoxide	41	1.100	+ 65	372
Methyl sulfide	52	0.846	-118	99
Methyl disulfide	68	1.055	-	243
Ethyl sulfide	35	0.837	-148	200
Thiophene	38	1.068	22	183
1-Thio 4-oxane	31	1.116	- 8	300
**1, 4-Dithian	53	Solid	+233	391
1,4-Dioxane (coolant)	0	1.033	+ 50	214

*Carbon disulfide and methyl sulfoxide at concentrations below 1% cause coke formation in gas phase. On occasion all other sulfur additives tested have eliminated all coking.

**Compound not yet tested.

Figure 2

Wellman & Bjerklie

DIOXANE ADDITIVE
FOR HIGH TEMPERATURES
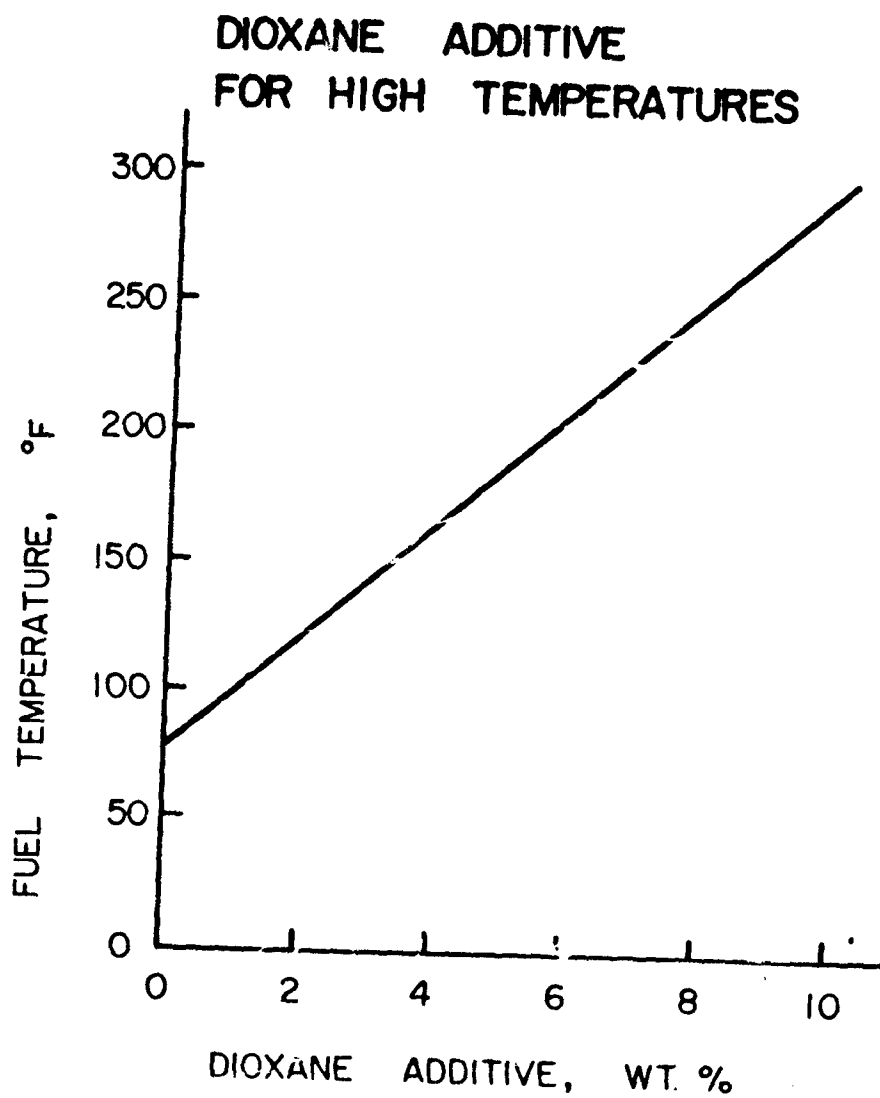
FIG. 3

Wellman & Bjerklie

EFFECT OF DIOXANE
ON IGNITION

FIG. 4

TEMPERATURE RISE OF IGNITER
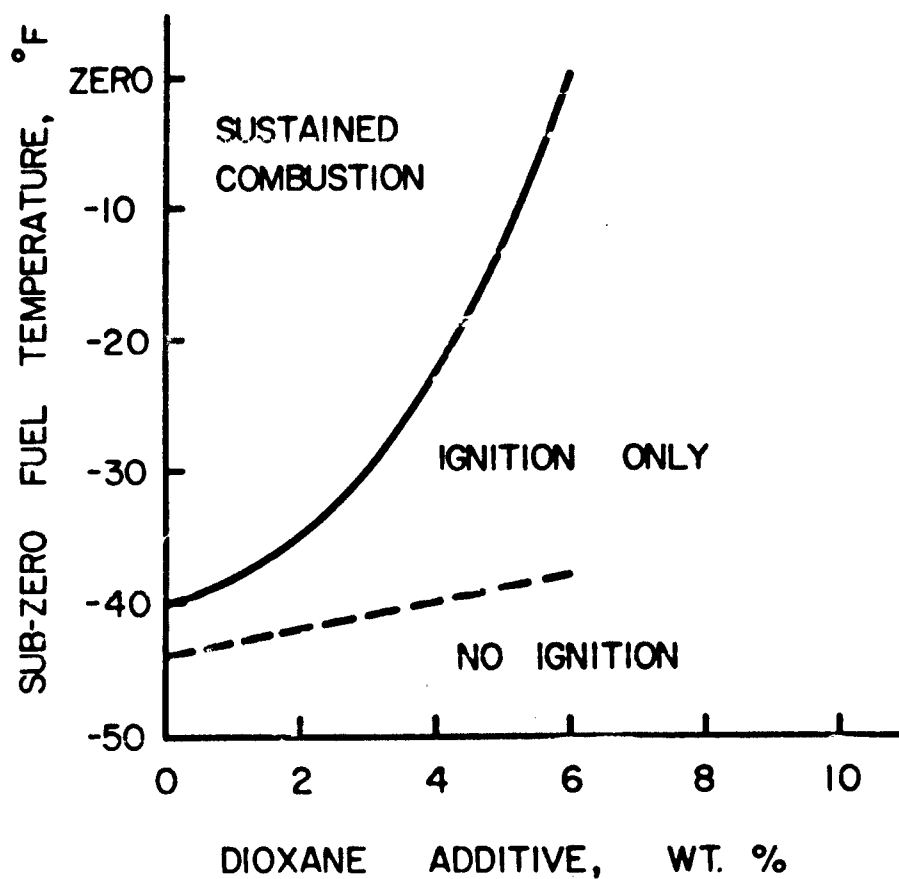
FIG. 5

Wellman & Bjerklie
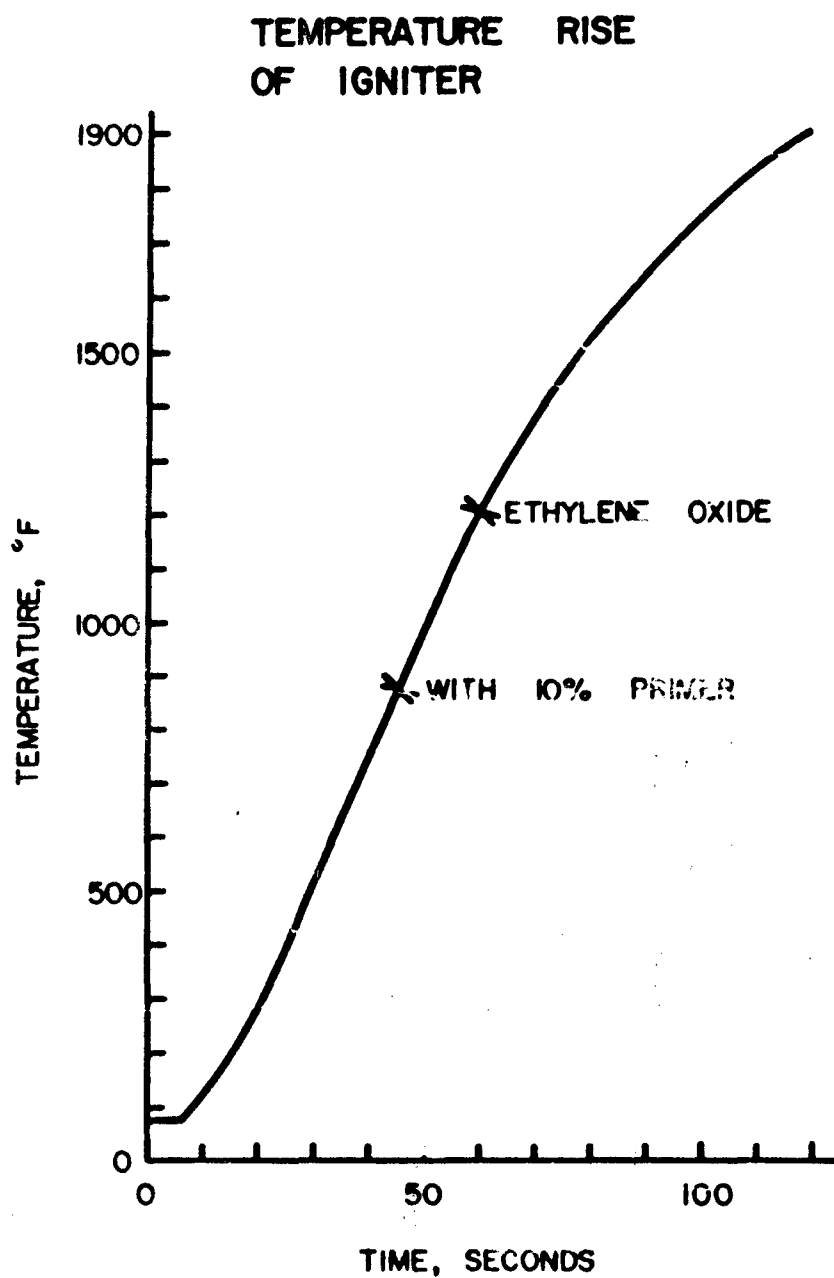
VORTEX GAS GENERATOR

EXAUST

INJECTOR
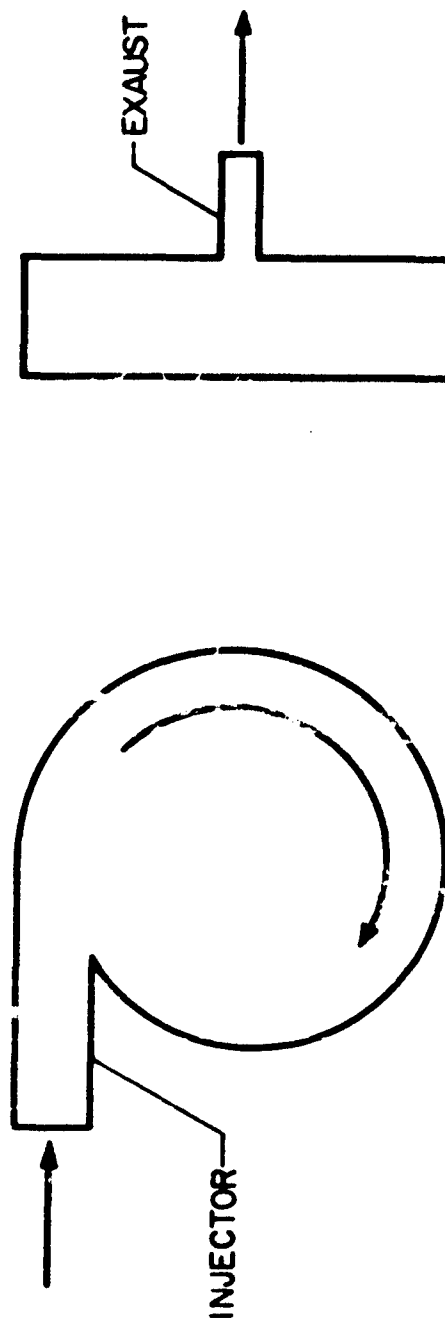
FIG. 6

GENERAL DISCUSSION

W. T. BARNES (Convair): I'd like to ask a question relative to the amount of water specified, 300 parts per million -- do you know whether any attempt is being made to incorporate that or a lower figure in the specification, which I understand is forthcoming for ethylene oxide?

MR. BJERKLIE: Yes.

PAPER

HIGH ENERGY FUELS IN AIR BREATHING ENGINES

by R. A. DeZubay & S. M. King
(Presented by Mr. King)
Curtiss-Wright Corporation

(See pages 349 to 356, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by W. T. Olson
(Presented by H. C. Barnett)
National Advisory Committee for Aeronautics

(See following pages, 125 to 133)

GENERAL DISCUSSION

None

Olson

Discussion Prepared by
Dr. Walter T. Olson
Chief, Propulsion Chemistry Division
Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics

on Dr. E. A. DeZubay and Dr. S. M. King Paper
HIGH ENERGY FUELS IN AIR-BREATHING ENGINES

Drs. DeZubay and King have outlined for us the heats of combustion of substances that might conceivably serve as high energy fuels, and, further, they have discussed some of the problems that might be expected to be encountered. I shall use most of my comment time to enlarge on some of the problems attendant on the use of boron fuels in engines.

Before making these specific comments on boron fuels, however, I wish to point out one factor involved in the use of hydrocarbon fuels that is an important one to consider for any fuel; that is, the ability of the fuel to serve as a coolant. Fuel cooling is already used for engine lubricant. Increasing cooling loads may include cabin, electronics, and even engine turbine and other engine parts as flight is pushed to higher Mach numbers. Figure 1 shows some fuels typical of those that the authors have considered. The heating values on a weight basis and the volume required to contain a given heating value are listed for JP-5, selected light hydrocarbons (SLH), methane, ethyldecaborane, and hydrogen. The last column lists cooling capability which is simply the sensible and latent heat that the fuel could absorb between a refrigerated state near its freezing point and a temperature where thermal degradation of one kind or another is encountered, or a reasonable upper limit of 1000° F; the value is expressed as percent of the heat of combustion. Ordinary jet fuels are limited by freezing point at one end and excessive gumming at the other end of the temperature scale. The temperature at which gumming becomes excessive depends on the batch of fuel, but some poor quality batches have already caused trouble in modern engines where the main heat being dumped into the fuel comes from the oil-fuel heat exchanger. Low molecular weight hydrocarbons, with methane as an outstanding example, can be refrigerated to much lower temperatures than jet fuels, can be heated to higher temperatures without thermal degradation, and have a slightly higher specific heat; thus they afford two to three times the cooling capability of current jet fuels (ref. 1).

The boron hydride fuels have more tendency to decompose at elevated temperatures than the hydrocarbon fuels. This poses a particular problem in their use. They will not be good refrigerants or heat sinks, and they may even have to be protected from excessive temperatures in fuel lines, nozzles, and so on. Indeed, we have found this to be the case in some of our experimental work with them.

To proceed with the discussion of boron fuels, however, the ultimate fuel that the authors have mentioned, ethyldecaborane or methyldecaborane, is not yet available in more than sample quantities. The experimental research pertinent to the use of boron fuels in engines thus can be considered to have been done with interim fuels. This research has been largely done by the NACA, and dates back to around 1949 or 1950 when not only diborane was being used in small-scale experiments, but attempts were being made to burn pure metals including boron metal as wires, powders or slurries of powder in hydrocarbons. Since 1952 the NACA, in cooperation with the Air Force and the Navy Department, Bureau of Aeronautics, has been able to continue with research on boron compounds, with pentaborane as the principal interim high-energy fuel. Some engine experiments have been conducted with borate esters which are low-energy fuels, but which do have boron in them. Some 30 reports on this boron fuels research are included in a summary (ref. 2). More than 20 additional reports have been published since reference 2. The latest review of the research in this area by NACA was presented the week before last at the Institute of Aeronautical Sciences Propulsion meeting in Cleveland (ref. 3).

To review here quickly the highlights from research on boron fuels, consider first, experiments pertinent to their use in turbine engines.

In early experiments, boron-containing fuels were burned in different jet-engine combustors with only minor modifications to them, and the deposit problem as revealed in this work is typified in figure 2. A series of experimental studies has resulted in several design principles that greatly alleviate this deposit problem. These principles, illustrated in one kind of combustor in figure 3, include extensive air filming, both in the upstream end and on the walls of the combustor to prevent deposition. Also, the fuel is air-atomized finely and fed air rapidly from all sides to avoid prolonged existence of rich mixtures; wall-wetting is avoided by controlled penetration. Jets of dilution air from long slots penetrate well and interweave and cross-diffuse to produce an acceptable outlet temperature distribution. It is considered now that high efficiency combustors for boron fuels with adequate pressure drop and temperature profile, and with relative freedom from deposits can be achieved. A picture of one such combustor that was evolved and tried on an engine is shown in figure 3. True, the combustion principles have been worked out on a volatile boron fuel, and

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a few preliminary tests indicate that a low volatility fuel such as ethyldecaborane with its very different properties will require some modification of these design principles. That is not surprising; the analogy would be to try to burn a light machine oil in a system designed to burn gasoline. We feel quite optimistic about the combustion part of the problem, however.

Another highlight of the research is that a particular kind of problem in the turbine part of the engine is encountered. The experience in running current gas turbine engines on boron fuels at simulated altitude is that the engines can be operated for a short period of time on boron fuel, and during this time practically all of the thermodynamic promise of the fuel is realized as improved specific fuel consumption. After only a few minutes, however, the performance of the engines noticeably deteriorates. Thrust begins to drop, and either the tailpipe of the engine must be opened, or the engine must be overtemperatured if rotational speed is to be maintained. This phenomenon has been encountered at simulated altitude both in engines with single-stage turbines and in an engine with a two-stage turbine. The thrust loss for each engine is shown in figures 5 and 6. In each case part of the loss is due to the thermodynamic properties of the exhaust gas. Continuing and increasing loss is noted throughout the run as turbine efficiency decreases. This efficiency loss is associated with the traveling waves of the viscous boron oxide that the authors alluded to, and with its general fouling of the stator and turbine. Some further loss is indicated as a tailpipe pressure loss; it results from too large a turbine-outlet Mach number and is a consequence of poor turbine efficiency.

The effect of these losses on specific fuel consumption is shown in figure 7. The engine was run on gasoline or jet fuel, and then the fuel was switched to pentaborane. The initial decrease in specific fuel consumption is almost that to be expected on the basis of heats of combustion. Reasons for the increase in fuel consumption with time were just discussed. With the nature of the problem known there are some things that can be done to alleviate it; the extent to which the problem can be alleviated cannot be predicted with certainty. It will require further experimental research when additional fuel for this work becomes available.

During the course of the program a single run in a full-scale afterburner was made with pentaborane fuel. There is no indication that this presents a severe combustion or deposit problem. Detailed engineering attention required will include keeping the fuel cool as it comes into the injector system in this hot end of the engine, and attending to design details around the variable area nozzles so that boron deposits do not freeze up the mechanism.

As in the case of the afterburner, experiments with ramjet combustion systems indicate that boron fuels will be relatively easy to apply to this kind of system. After a number of experiments in ducts

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to devise a $9\frac{3}{4}$-inch diameter combustion system, several ramjet powered flights were made with boron fuels. In three of the flights, the engine was started and then dropped from a carrier airplane. The fourth flight was rocket boosted. Mach numbers obtained on these flights ranged up to $3\frac{1}{4}$ (fig. 8). Altitudes were of the order of 30,000 to 40,000 feet. Eight channels of telemetering reported back the performance of the engine, and perfectly satisfactory combustion apparently was obtained. Also, a few short runs of pentaborane have been made in a 48-inch diameter ramjet engine for one of the country's guided missiles; this was purely an experimental or exploratory study.

The problems attendant on the reactivity of boron fuels with air and with water, on their toxicity, on the disposal of the boron oxide exhaust, and on the thermal decomposition of the fuel have been properly mentioned by the authors.

In summary, the boron fuels are still very much in the research stage. The degree of success with which all of the problems associated with their use can be met is not known. Although there is a large degree of optimism over a number of these problems, considerable additional experimental research is required. The military services are continuing with proper vigor to have pilot plant and experimental quantities of fuels prepared so that this research can go forward.

As a final comment I should like to point out that, while the use of free radicals as fuels, and even ions as fuels, is very appealing when one looks at tables of their energy content, the real point here is that we do not know scientifically whether such materials can be made to exist in concentrations of interest and with a minimum or kind of equipment that d es not, through its weight or complexity, throw away the thermodynamic advantage seen in those fuels. Here the engineer would do well to wait until the scientist has produced those breakthrough ideas which will indicate what should be done. I am not at all to be construed as being against research on these blue sky ideas. But I do recognize a tendency to gallop ahead prematurely into engineering developments on ideas where research has not indicated the solution to certain barrier problems, or even if solutions are possible. The authors have done well to stimulate our imagination, however.

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   Jet Fuels. ASTIA Document No. AD119634, March 1957.

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FUEL PROPERTIES

Figure 1

DEPOSITS IN TURBOJET COMBUSTOR
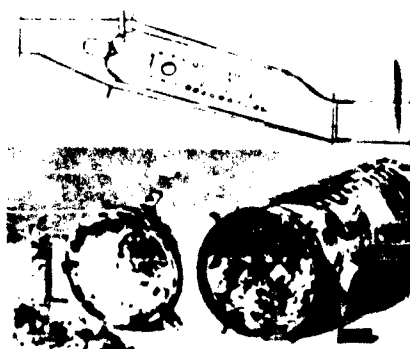
Figure 2

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FEATURES OF AN ANNULAR COMBUSTOR FOR BORON FUEL
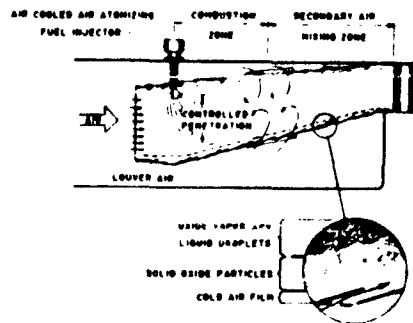
Figure 3

APPEARANCE OF COMBUSTOR FROM
FULL-SCALE ENGINE AFTER BURNING
150 POUNDS OF PENTABORANE
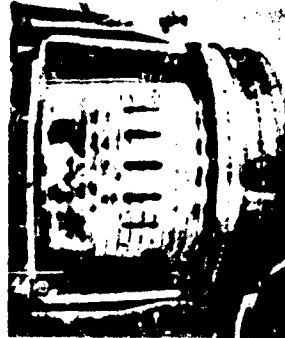
Figure 4

**NET THRUST LOSS
WITH SINGLE-STAGE TURBINE ENGINE**

FUEL, PENTABORANE
SIMULATED ALTITUDE, 50,000 FT
SIMULATED MACH NUMBER, 0.8

Figure 5

**NET THRUST LOSS
WITH TWO-STAGE TURBINE ENGINE**

FUEL, PENTABORANE
SIMULATED ALTITUDE, 50,000 FT
SIMULATED MACH NUMBER, 0.8
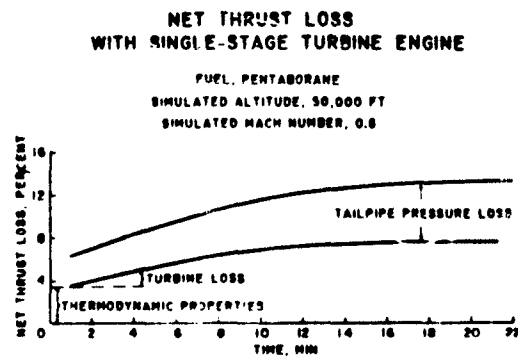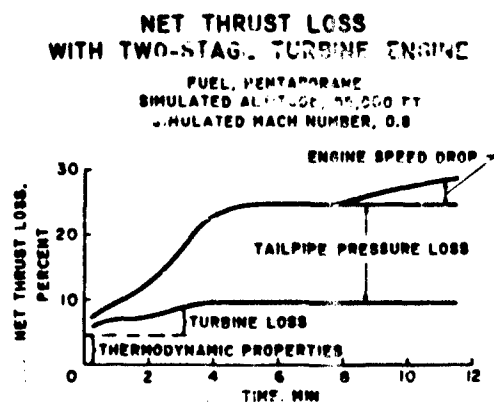
Figure 6

SPECIFIC FUEL CONSUMPTION OF
TWO TURBOJET ENGINES WITH PENTABORANE

SIMULATED ALTITUDE, 50,000 TO 55,000 FT
MACH NUMBER, 0.8
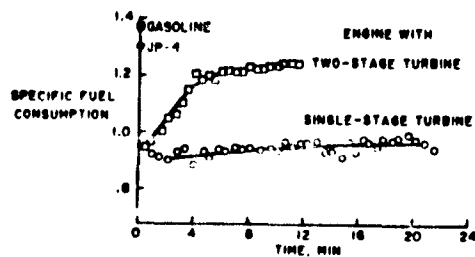
Figure 7
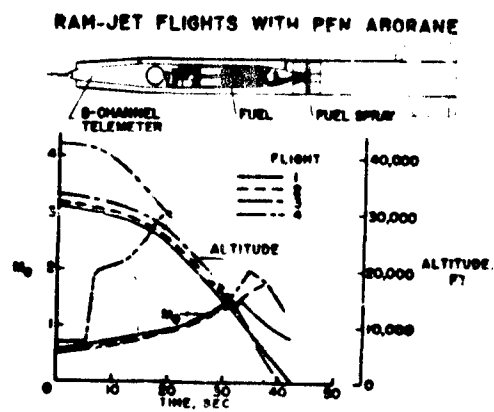
RAM-JET FLIGHTS WITH PEN ABORANE

Figure 8

PAPER

COMPARISON OF LOX/KEROSENE, LOX/HYDRAZINE, AND
FLUORINE/HYDRAZINE AS PROPELLANTS FOR LONG-RANGE ROCKETS

by H. H. Koelle and J. G. Tschinkel
(Presented by Dr. Tschinkel)
Army Ballistic Missile Agency

PREPARED DISCUSSION

by H. F. Dunholter
(Presented by D. H. Stewart)
Convair-Astronautics, A Division of General Dynamics Corp.

Dunholter

Discussion Prepared by
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on H. H. Koelle, J. G. Tschinkel Paper
COMPARISON OF LOX/KEROSENE, LOX/HYDRAZINE, AND
FLUORINE/HYDRAZINE AS PROPELLANTS FOR LONG-RANGE ROCKETS

Mr. Koelle and Dr. Tschinkel have presented a very good
method of comparing propellant performance. The use of "capacity fac-
tor" for weight, and vertical ascent for range results in a simplified
but effective comparison method. The more rigorous range calculation
appears to be based upon a constant thrust for the different propellants
rather than a constant initial thrust to weight ratio, and therefore is
difficult to compare with the ascent range data.

The authors' apparent enthusiasm for Fluorine/Hydrazine is
more controversial. The performance potential of the propellant is very
great because of its high bulk density and high specific impulse, but
it is not obvious that this performance can be realized in practice.
The propellant has a very high gas temperature ($7000°F$) at optimum mix-
ture ratio and hydrazine as a coolant is limited by its disassociation
characteristics. Hydrazine also has a high freezing point ($35°F$).
Additives used to lower its freezing point and to increase its stabil-
ity as a coolant may have an appreciable effect on its performance
potential. These questions can only be answered by research and it is
hoped that the experimental data will be available soon.

The present study has been limited to single stage vehicles.
If the study were extended to upper stage vehicles, other propellants
would show to advantage particularly those with good cooling character-
istics which permit the use of large area ratio nozzles.

There are, of course, numerous other factors to be considered
in the selection of a propellant for a weapon system other than that of
the effect on the gross weight and size of the rocket. For example,
both the development time and cost of the weapon system can be appre-
ciably affected by the choice of propellant. Such primary factors can
not, however, be generalized but can only be considered in the light of
the state of the art and available facilities at a given time period.

GENERAL DISCUSSION

DR. TSCHINKEL: I am glad to still have this chance to fire back. First of all, I will gladly accept the charge to be enthusiastic for this fluorhydrazine propellant. I believe we would not have any propellant if some people had not been enthusiastic for it.

Then, to the various points I would say this -- it may be more adequate in general terms to compare missiles at constant acceleration instead of constant thrust, but practically, what you are faced with mostly is that you have a rocket engine on the market of a given thrust and you look out for what you can do with this engine. This is the very thing we did here.

Secondly, as to the use of hydrazine as a coolant, you have heard this morning supporting evidence from Jet Propulsion Laboratory that hydrazine is one of the best coolants that you can have. Just to give one figure that I remember from what Mr. Barts told us, you saw on his table most common propellants had burned-out fluxes around 10 Btu/in.^{2} sec whereas Jet Propulsion Laboratory could reach 20 with hydrazine in some simulation tests. And there is no appreciable breakdown of the hydrazine expected during the short exposure it goes through when passing through the cooling jacket.

There have been small scale regenerative cooling tests years ago, and programs are under way to demonstrate now this cooling capability in more actual motor tests.

As to the freezing point of hydrazine around 0°C, we do not worry about this at all. We are concerned with long-range rockets where you handle bulks of tons of the propellants, and any calculation of heat transfer can show you that it takes days to freeze a container with some insulation around it of such large quantities. Besides, any operation of this size always has heating equipment on hand, with some warm air blowers or other means to keep the liquid from freezing.

Regarding the other non-technical viewpoints that my critic mentioned for the selection of a rocket propellant, of course, those are acknowledged and are present, and it is certainly always a matter of compromise with the application in mind. As we see it, the merits of this system would be mainly in very long-range rockets and in second-stage rockets because light weight is of great importance there, since it greatly reduces the mass of the booster.

As to the use of the capacity factor, I wanted to give credit to Jet Propulsion Laboratory as they also use this and I am not sure where the priority is. It goes back over several years.

MR. STEWART: I would like to congratulate Dr. Tschinkel for not giving up the fight. He has, as Dr. Dunholter mentioned, a good comparison method. However, let's take some of the points that were brought up by Dr. Tschinkel and evaluate them.

First, Dr. Tschinkel mentioned that the comparison on thrust
level appeared to be valid because "we have an engine and we just go
out and use this." Unfortunately, the engine has to be built. It was
built, initially, because of a preliminary design study which investi-
gated engine thrust requirements (for various propellants) for a
specific application. These engines and missiles are tailored to
system requirements. The days when you design a structure, shove an
engine into it, and then wait to see what you get are pretty much over.

Let's take the regenerative cooling characteristics of hydra-
zine. It admittedly has an excellent potential, as Mr. Bartz points out.
It compares favorably with water. However, when you look over this
cooling potential, you discover the cooling characteristics of hydrazine
are such that your wall temperature will have to be maintained around
500° to 600°F. You have combined this fuel with an oxidizer which
yields temperatures of the order of 7000° to 8000°F, depending upon the
mixture ratio you have selected. This gives a very healthy heat trans-
fer problem. This can be overcome in an engine which is large enough
that the regenerative cooling capacity or the coolants are capable of
soaking up this heat. For some applications, however, this means that
you are going to have to chase these coolants through the cooling coils
at such high velocities that the pressure drops are terrific. This,
for example, imposes a design and weight problem upon the turbopump.

To look at another aspect of hydrazine, the freezing character-
istics; if you have to provide a nursery for each of the missiles you
design, it is going to increase the weapon system cost. You can put
additives in the hydrazine in order to reduce the freezing point --
two of the best I can think of will bring the freezing point down to
about -50° to -60°C. One of these is ammonia. The other is hydrogen
cyanide. With hydrogen cyanide you aggravate the toxicity problem;
also, the specific impulse is degraded. Incidentally, fluorine-ammonia,
compared with fluorine hydrazine at the same pressure, would yield 296
seconds specific impulse, whereas hydrazine would give about 300 seconds
under the same conditions. If it is necessary to add, for instance,
ammonia to the hydrazine, in order to control the freezing point, you
have now degraded the specific impulse to the point where you should
have started with ammonia initially. I am not proposing ammonia as a
panacea. Ammonia is not the world's greatest coolant, but you can cool
with it, and you do avoid the freezing problem of hydrazine, while
sacrificing only about 1.3% specific impulse.

MR. BARTZ: It is extremely difficult for me to follow
Mr. Stewart's reasoning relative to the selection of ammonia rather
than hydrazine as a high-energy-system fuel. He starts by conceding
that our experimental evidence shows hydrazine to be a very good coolant
but quickly arrives at the point where he fears that extreme coolant
velocities will be needed because of expected extreme heat fluxes.
This conclusion cannot be reached, however, without specifying the
operating chamber pressure. For chamber pressures near 300 psi, our
data indicate that normal velocities should be adequate, whereas only

for considerably higher chamber pressure operation will excessive cooling velocities be needed.

Mr. Stewart complains of the need for an expensive "nursery" for each missile because of the high freezing point of hydrazine and suggests ammonia as an alternative fuel. It seems to me that it is inconsistent to be overly concerned with the possible necessity of keeping the fuel no more than 100°F above ambient while utilizing liquefied gas oxidizers having boiling points several hundred degrees below ambient temperature which necessitate extensive insulation or even refrigeration in order to maintain boiloff rates acceptably low. If he has apprehensions about the cooling capabilities of hydrazine, he should multiply these apprehensions by about a factor of three for ammonia, since, in addition to much lower values of q_{all}, for ammonia under similar flow conditions, the permissible bulk temperature rise for ammonia is also much lower, thus restricting the surface area that can be cooled. Furthermore, it is difficult to see where freezing point is going to be an important factor in the applications for which the high-energy systems might be used.

Our experimental measurements have shown that even up to wall temperatures approaching 1000°F the hydrazine does not decompose in our tubes in which coolant velocities are varied between about 30 and 90 ft/sec. Even a very slight amount of decomposition would show up in our tests as a sizable error in the heat balance because of the large heat of decomposition of hydrazine. No such heat balance errors have been observed.

MR. BRYAN: I would like to compliment Dr. Tschinkel on his paper. There are several things I would like to bring up concerning it. He did not mention nitrogen trifluoride and should have. This material does have properties so far superior to fluorine in handling that the small sacrifice in the specific impulse could be tolerated. You might be able to cool with nitrogen trifluoride.

Another thing concerning the comment of Mr. Stewart that the freezing point of hydrazine would have to be lowered, there are very light-weight insulators these days. I wonder if we are not giving overemphasis to the freezing point as a requirement. This weapon could be loaded very rapidly before use and fired with little delay. Normally, they are not stored loaded. I doubt if you would require a freezing point lower than that of hydrazine.

DR. TSCHINKEL: Just another quick point about the freezing point, we do not consider putting in any additives because they all would subtract from performance. We really do not consider this a serious problem and I would not consider heating equipment in the field as a "nursery." Besides, you have soldiers all around who do not want to freeze in the Arctic weather and you have heating equipment around.

As to the nitrogen trifluoride, I cannot say anything about that. We have not considered it. One of the points we made was that the propellant must be currently in production. Nitrogen trifluoride is not as yet.

PAPER

STUDIES WITH TWO-STAGE ROCKET ENGINES

by Anthony Briglio, Jr.
Jet Propulsion Laboratory, California Institute of Technology

(See pages 358 to 377, Volume 1, PFL 212/13)

PREPARED DISCUSSION

by Edward B. Greenberg
Reaction Motors, Inc.

GENERAL DISCUSSION

None

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Discussion Prepared by
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on Anthony Briglio, Jr. Paper
STUDIES WITH TWO-STAGE ROCKET ENGINES

The investigation of two-stage rocket engines carried out
at JPL has produced some valuable and highly promising results. The
conclusion that both smooth combustion and high performance can be ob-
tained with several propellant combinations in a rocket engine utiliz-
ing the jet mixing scheme of injection is in agreement with the re-
sults of a similar investigation carried out at RMI (Ref. 1). This
study also established the design parameters affecting the jet mixing
processes and the effect of these parameters on thrust chamber per-
formance. The following comments are made in the light of knowledge
gained from this investigation.

One of the features of a jet mixing injection system is the
possibility of simplified injector design compared to more conventional
injectors. The preparation of propellants prior to combustion (mixing,
atomization, etc.) is usually dependent in a conventional injector
(e.g. impinging stream or spray type) upon the impingement of liquid
propellant streams. The design and manufacture of injectors is often
complex and costly. Also, a new injector must be designed for each
new rocket configuration or propellant combination. In contrast to
the conventional injector, the processes of atomization, vaporization,
mixing and heating in the jet mixing injector are accomplished by the
mixing of the liquid propellants (second stage) by the hot gas jet
(first stage). Liquid propellant injection can therefore be greatly
simplified.

It seems that the designs of the JPL two-stage engines have
not taken full advantage of the technique of jet mixing injection. By
employing triplet sets of orifices to inject both the first and second
state propellants some of the complexity of a conventional injector
has been retained. High performance has been obtained with RMI two-
stage engines utilizing a considerably simpler injection scheme. The
second stage injector consists of a cylindrical section through which
the high velocity hot gas jet (first-stage combustion products) is

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passed. This section consists of two spools, one for fuel injection and one for oxidizer injection. The second-stage propellants are injected radially inward into the gas stream through equally spaced holes located on the circumference of the spools. The plane of injection of the fuel was upstream of the oxidizer injection. High performance (95 to 100% of theor. C*) has been achieved even when few large diameter injection orifices (2 fuel and 4 oxidizer holes with dia. = 0.316 in.) were used at a 5000 lb. thrust level.

The investigation carried out at RMI has recognized that the performance of a two-stage rocket engine is a highly complex function of a multitude of variables. Since the design parameters affecting thrust chamber performance are interdependent, the result of varying any one cannot be simply determined. In order to determine the effect of any one parameter cognizance must be taken of this multiple variation and interrelation of parameters. This was accomplished by utilizing the methods of dimensional analysis and multiple regression analysis (Ref. 2) to formulate and evaluate an empirical equation which describes thrust chamber performance in terms of seven dimensionless parameters.

The parameters which were varied in the JPL investigation are the fraction of propellant burned in the first stage, gas velocity in the mixing jet, the engine L* and the orifice pressure drop. Since, as mentioned above, these parameters cannot be individually varied their effect on thrust chamber performance cannot be determined as readily as has been attempted during the JPL study.

The low performance of one 1000 lb. thrust engine has been attributed to the fact that the gas stream velocity was reduced from 600 ft/sec to about 200 ft/sec or less. The actual cause may not be this simple, since several configurational and operational changes were made in order to effect a decrease in the jet velocity. First, as a result of eliminating the inter-stage nozzle the condition of sudden enlargement between nozzle throat and main-chamber diameter was eliminated. This probably reduced radically the intensity of recirculation within the main chamber – a factor which could be more significant than a change in nominal axial velocity. In addition, the percentage of propellant injected into the first stage was increased to several higher values. Therefore, since there has been a multiple variation of parameters affecting performance, a decrease in performance cannot clearly be attributed to only one of these changes (decrease in gas stream velocity).

It is reported that a reduction in main chamber L* from 44 in. to 24 in. resulted in a negligible loss in the performance of a 1000 lb. thrust engine operating on SFNA-DETA. Although it might have been expected that a decrease in L* would cause a loss in performance it should be noted that the reduction in L* was achieved by two configurational changes. The chamber to throat area ratio was decreased from 4:1 to 2:1 and the chamber aspect ratio (L_{ch}/D_{ch}) was

141

doubled. Each of these changes could cause an increase in performance (Ref. 1, 2) thus nullifying the effect on performance of decreasing L* as such.

The result of attempting to scale up from 1000 lb. thrust to 20,000 lb. thrust was lower performance at the higher thrust level. A similar investigation was carried out at RMI (Ref. 1) whereby a 35,000 lb. thrust engine was modelled after a 5000 lb. thrust engine. Using an empirical equation established for the small scale (5000 lb. thrust) engine, the performance level of the large scale powerplant was predicted. Here, too, the performance of the large scale unit was lower than expected. Further analysis disclosed that the homologue was actually distorted from the model in that some of the design parameters had been varied. Had proper distortion factors been taken into consideration the low performance of the large scale unit could have been predicted. Perhaps the low performance of the JPL 20,000 lb. thrust engine was also caused by distortion from the model. Although it is difficult to perceive the basis for scaling because of the limited description of the configurations and operating conditions, it appears that even though the general layout of the model and homologue is identical several distortions between the two do exist. In addition to the differences already noted, the following changes were made in scaling up.

1. The aspect ratio of the main chamber was almost halved.

2. The mass velocity in the main (second-stage) chamber was doubled.

3. Although the propellant flow rate was increased by a factor of twenty, the flow rate per triplet was increased by a factor of ten since the number of triplets was doubled.

It appears, then, that the low performance of the large scale engine may not have been caused by any inherent characteristics of the powerplant, but rather was a result of scaling distortions.

Our comments should be taken basically as efforts to supplement the insights obtained by the authors into the subjects of injection and scaling - two subjects in which we all know much more insight is needed.

CONFIDENTIAL

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COMMANDER TRUAX: I would like to express our thanks to all the participants -- particularly to the authors and reviewers. I would also like to say that a program such as this does not fall together by itself. It takes a lot of hard work to do it, and I would like to extend the thanks of the participants to Don Brooks and to Ruth Adams for the great deal of work that they have done in getting this session organized.

MR. BROOKS: Thank you. I would like to express the deep appreciation of the staff to all of you for your excellent cooperation. We've enjoyed having you.

The following papers were presented at the symposium but were not received in time to be included with the preprints (Volume 1, PFL 212/13):

AN EVALUATION OF LIQUID OZONE-OXYGEN MIXTURES
AS ROCKET OXIDIZERS

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Princeton, New Jersey

For almost three years the authors and others in the Department of Aeronautical Engineering at the James Forrestal Research Center, Princeton University have been engaged in an evaluation of liquid ozone-oxygen mixtures as rocket oxidizers from theoretical and experimental standpoints including thermochemical calculations of performance, handling of the mixtures in a pilot plant scale generation system and a pressurized rocket system and preliminary determination of actual performance in a small rocket motor. The experimental effort has been limited to the mixtures containing up to 25% ozone by weight.

In response to a request by the Rocket Propellants Section, Wright Air Development Center of the United States Air Force the University submitted a proposal which resulted in Confidential Cost Contract No. AF 33(616)-2411 and work was begun on 1 April 1954. A reasonably detailed history of the work since that time can be found in the Quarterly Progress Reports of the above contract (1). Opinions and facts obtained over the period of this work are presented in the following paragraphs.

DISCUSSION

Our efforts have been organized and reported under a work statement that incorporates the headings which are used below in presenting the discussion:

Bibliography

The major bibliographic effort on ozone has been produced by the Armour Research Foundation (hereafter ARF) (2) while our effort has been limited to those references that concern the use of liquid ozone-oxygen mixtures as rocket oxidizers. The results of

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this effort were published in unclassified and classified sections of
a preliminary selective bibliography as Appendices of the Fourth
Quarterly Progress Report (I).

Properties of ozone as recorded in the available
references are summarized on Table I along with corresponding oxygen
properties. Primary sources of this information which contain much
more detailed information are reports by ARF (3) and the Linde Air
Products Company (4). The important property of ozone stabilization
is treated in a United States Patent issued to C. E. Thorpe, et al (5)
based on their work over a considerable period at ARF.

Theoretical Thermochemical Performance Calculations

Since data on the theroretical performance of ozone were
sparse and conflicting, and almost totally absent for liquid ozone-
oxygen mixtures, a considerable program of thermochemical calculations
was undertaken on an IBM-CPC digital computer using a modification of
the method developed by Huff and others at the NACA Lewis Flight
Propulsion Laboratory. Calculations for the performance of these
mixtures from 100% liquid ozone in 25% decrements to 100% liquid
oxygen were made for a number of fuels at 20, 40, and 60 atmospheres
chamber pressure for frozen equilibrium and sea level exhaust.
Graphs for ethyl alcohol (95%)-Water (5%), unsymmetrical dimethyl
hydrazine and liquid hydrogen are included herein as Figures 1
through 27. They show plots of effective exhaust velocity, adiabatic
combustion temperature, average specific heat ratio, average molecular
weight and mole fraction of the combustion products versus mixture
ratio. Further calculations of liquid hydrogen for shifting
equilibrium have been started and several hydrocarbon fuels will
probably be calculated later.

Handling Tests

A laboratory was constructed at Forrestal Research Center
specifically for the purpose of testing quantities of liquid ozone-
oxygen mixtures up to a few pounds. It was equipped with protective
walls, provisions for remote viewing, and exhaust blowers to permit
the conduct of four kinds of tests that were pertinent to the handling
characteristics of the mixtures. The handling experiments were
characterized as quality, detonation, pressure and venting sensitivity,
and flow tests.

Raw materials used in generating liquid ozone-oxygen
mixtures consist primarily of gaseous and liquid oxygen. Freon 13
and helium also come in contact with the mixtures. The hydrocarbon
content of these substances was measured in terms of parts per
million of CO_2 as indicated on a Liston-Becker continuous, single
wave length, spectrophotometer analyzer. For lack of a tested
figure of significance a limit of twenty parts per million of CO_2
was placed on the hydrocarbon content of the gases.

CONFIDENTIAL

Layton, Glassman, & Garvin

TABLE I

Properties of Ozone and Oxygen
Pertinent to their Use as Rocket Oxidizers

Property	Ozone	Oxygen
Molecular Weight, lb/lb mol	48	32
Boiling Point, °F	-169.4	-297.3
Melting Point, °F	-314.9	-361.1
Critical Temperature, °F	+10.2	-181.8
Critical Pressure, lb/in^2	802.4	730.4
Critical Density, lb/ft^3	30.0	26.8
Critical Volume, ft^3/lb mol	2.4	1.2
Gas Density (32 °F, 14.7 lb/in^2) lb/ft^3	0.13	0.086
Liquid Density (-169.6 °F) lb/ft^3	91.1	
(-297.3 °F)	98.1	71.2
(-319.6 °F)	100.8	
Surface Tension (-297.3 °F) lb/in^2	219x10^{-6}	75x10^{-6}
Liquid Heat Capacity (-169.4 °F) Btu/lb mol °F	17.0	13.0
Gaseous Heat Capacity (77 °F) Btu/lb mol °F	9.4	
Thermal Conductivity (-297 °F) Btu/hr ft °F	0.07	0.09
Liquid Viscosity (-297 °F) lb/ft sec	23.0	2.8
(-320 °F)	62.5	
(30% O$_3$ - 70% O$_2$ by wt.)	4.6	
(9% O$_3$ - 91% O$_2$ by wt.)	5.2	
Heat of Vaporization (at B.P.) Btu/lb	136	91.6
Liquid Magnetic Susceptibility ft lb sec units/lb (x 10^6)	63x10^{-3}	109
Dielectric Constant (ref: vacuum = 1.00)	4.75	1.46
Heat of Formation, H(25°C) Btu/lb mol	-61,900	0

Phase Boundaries, Ozone-Oxygen System
        at -297.3°F   29.3 and 72.4% O$_3$ by wt.
        at -319.6°F   9 and 90.8% O$_3$ by wt.

CONFIDENTIAL

The "quality" of the gaseous ozone produced was measured by a method developed at ARF. After a considerable number of operational difficulties, the equipment which was purchased from them was used to ascertain that the quality of the gaseous ozone generated at Princeton was equivalent to that used at ARF.

Detonation tests were conducted to show the character of such reactions involving ozone and to test our safety provisions. The detonations were initiated most satisfactorily by fusing a wire immersed in a concentrated liquid ozone sample. They confirmed the highly brisant character of such ozone reactions.

Pressure and venting sensitivity tests were run using specially designed stainless steel vessels. The liquid ozone (25%)-oxygen (75%) mixtures were demonstrated to be insensitive to pressurization with helium up to 1000 lbs. per square inch and to rapid venting, although this latter conclusion has been modified somewhat as described later. A method of measuring liquid level and concentration in the closed vessels based on the specific gravity difference between ozone and oxygen using differential pressure manometers was tested in this operation and accepted for use in the pilot plant scale generation system somewhat prematurely as indicated by subsequent experience.

Flow tests were conducted with sufficient success to indicate that the 25% ozone mixtures could be used with more or less conventional rocket design concepts. Here again more careful and thorough testing in the laboratory would probably have saved time in operating the larger pilot plant type systems.

Overall Stability Tests

Reports of the major workers in liquid ozone indicate, and our experience confirms that it is possible to develop techniques for the safe generation, storage, and transfer of liquid ozone-oxygen mixtures in the laboratory. The primary factors in this success are the careful purification of the oxygen raw material, employment of compatible materials and substances, and the use of a thorough surface preparation procedure. A certain amount of cryogenic technique is also required. Experienced workers are therefore now able to deal with ozone in the laboratory without unexpected detonations. Purification of the oxygen is still receiving considerable attention from research workers from process, testing, and instrumentation standpoints. Table II gives a list of the compatible substances as tested and approved by ARF. Efforts are being made to increase the number of substances on this list, especially sealants. The surface preparation procedure currently employed at Princeton is shown in Table III. Continued development of this procedure is necessary to make it more effective and to reduce unnecessary operations. The procedure as shown was developed particularly for cleaning metal. A laboratory procedure

CONFIDENTIAL

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TABLE II

List of Materials and Substances Compatible
with High Concentration Liquid and Gaseous Ozone[*]

Aluminum Alloys[**] - 2S, 3S, 24S, 52S, 61S
Stainless Steels[**] - Types 302, 304, 316, 410, 416
Pyrex
Kovar
Teflon (purified)
Kel-F
Lubricants and Sealants. The utmost care is to be observed
        in using clean applicators, replacing caps, etc.,
        to prevent contamination of these substances:
            (1)   duPont FCD-441
            (2)   Halocarbon stopcock grease
            (3)   Flurolube and Halocarbon Oils
            (4)   Gilbreth #18 thread sealing compound
            (5)   Hoke "Slic Seal"
        Although not approved by ARF powdered purified teflon
        dispersed in deionized distilled water can be used as
        a pipe thread sealant where necessary especially for
        high pressure service, but the joint must be carefully
        cleaned and passivated by the regular surface preparation
        procedure.
Handy Andy Brazing Flux[**]

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[*] Use of these substances is based on tests and recommendations of
the Armour Research Foundation.

[**] When joining metals use inert gas shielded arc welding where
possible; alternatively, silver brazing, both high and low
temperature, using Handy-Andy flux is acceptable but the joints
must be cleaned before and after by the approved procedure.

CONFIDENTIAL

TABLE III

Surface Preparation Procedure for Liquid Ozone-Oxygen Mixture Service

1. Disassemble all parts not permanently fastened together.
2. Remove any major accumulations of oil, grease, or other contamination by using a plastic scraper and/or wiping with a cloth or paper towel.
3. Soak in 25% nitric acid for 15 minutes. Easily attacked aluminum alloy parts need not soak for full time.
4. Rinse thoroughly with tap water, then scrub with a stiff brush until all visible foreign material is removed.
5. Wash by submerging in warm (90 - 100°F) 5% solution of Lakeseal detergent in distilled water.
6. Rinse thoroughly with distilled water.
7. Dry with clean, hot (200°F) oxygen gas.
8. Soak in unused reagent grade carbon tetrachloride for 15 minutes

NOTE: Subsequent steps must be accomplished without touching ozone exposed surfaces except with stainless steel tongs that have been cleaned by this procedure.

9. Drain carefully and dry thoroughly with clean, hot (200°F) oxygen gas.
10. Reassemble component and seal all opening with aluminum caps and plugs which have been cleaned by this procedure and kept in clean air-tight polyethylene bags that are resealed after each opening.
11. After assembly of parts into system:
    (a) Dry system by circulating clean, hot (200°F) oxygen gas for 30 minutes,
    then (b) Passivate by:
    (1) Circulating low concentration gaseous ozone-oxygen mixture from the ozonator at 2 to 4 percent ozone through the system for 8 to 10 hours,
    (2) Seal system with the mixture inside for 12-16 hours.
    (3) Purge with clean, hot (200°F) oxygen gas for 30 minutes and then seal all external openings.

NOTE: Steps 1 through 7 do not need to be repeated for items removed briefly from the system for inspection or adjustment unless the possibility of contamination with oil, grease, or other non-compatible substances exists

CONFIDENTIAL

primarily for glassware may differ especially in the preliminary cleaning substances. Until the teflon dispersion described in Table II was found for use as a high pressure sealant severe galling of both alluminum and stainless steel threaded components and fittings resulted from use of the surface preparation procedure.

It is necessary to develop much more satisfactory tests of **overall stability of ozone and its mixtures. Efforts in this** direction have been made by the Air Reduction Company (hereafter AIRCO) in which they subjected liquid ozone mixtures to controlled spark discharges. Their early efforts under Princeton subcontract are described in Appendix A to the Seventh Quarterly Progress Report (I). Subsequent work has been carried out under direct Air Force sponsorship. The development of instrumentation techniques for measuring the order of one part per million of foreign substances in ozone-oxygen mixtures is critically needed. Some extension of the spectrophotometric technique adapted to measure with more sensitivity and other contamination than equivalent hydrocarbon content may be indicated.

Reaction Initiation Tests

One of the attractive possibilities of using liquid ozone-oxygen mixtures is the hypergolic initiation of reaction with certain fuels. Evaluation of this possibility may be necessary if we are ever to initiate combustion directly on the ozone mixtures. Current practice at Princeton involves starting a rocket run on liquid oxygen using a solid propellant igniter and switching to the ozone mixtures during the run and back again to the liquid oxygen prior to shut-down. This technique has been quite successful. Tests of various other methods of reaction initiation have been deferred.

Combustion Involving Ozone

Chemical kinetic studies of gaseous ozone with various fuels and reaction intermediates have been undertaken by one of the authors (Garvin) in the laboratories of the Chemistry Department. This work was previously supported by the Air Force on Contract AF 33(038)-23976, but has recently acquired Air Force Office of Scientific Research sponsorship. Details of the reaction of gaseous ozone with ethyl alcohol and ethylene oxide have been studied and work on the ozone-hydrogen reaction is currently underway. It is hoped that the results of this work can be correlated with rocket motor tests especially the combustion efficiency and stability limits.

Component and System Evaluation

It was decided that the experimental operations involving approximately 20 pounds of the 25% ozone-oxygen mixture required a

CONFIDENTIAL

CONFIDENTIAL

specially designed test cell. Figure 28 is a photograph of the
Ozone Evaluation Facility at Princeton. The mixture tank is
located directly behind the open rocket cell which Is seen in the
photograph. Slanted walls of reinforced concrete having minimum
12" thickness were used in the design of this building. Direct
viewing of neither the mixture tank nor the rocket motor is
provided from the control room on the far side of the facility
because of safety considerations. Mirrors are currently used but
not with complete satisfaction.

Revision No. 2 of the liquid ozone-oxygen mixture
generation and rocket systems is shown on the flow diagram of
Figure 29 and as is readily seen there are too many components to
point them out individually in this paper. The liquid oxygen supply
and vaporizer are located on the left side of the diagram.
Following across to the right, the ozonator can be seen in the
upper part of the next section. The sampling system and quality
test box have been subsequently removed as described below. The
.'quid oxygen and fuel tankage are conventional rocket test
installations.

It is the liquid ozone-oxygen mixture tank and its
accompanying complex of components and piping that is the heart of
the generation and rocket systems. The liquid ozone-oxygen mixture
generation system was designed by AIRCO and furnished on subcontract
to Princeton. It is described in some detail in Appendix D of the
Princeton Fourth Quarterly Progress Report (1). The Mixture tank is
seen to be a triple tank, the inner one contains the liquid ozone-
oxygen mixtures, the surrounding tank is the refrigerant jacket, and
the outer one is the vacuum jacket. The gaseous, low concentration,
ozone-oxygen mixtures from the ozonator (2 to 4% O_3) are passed
through a heat exchanger and bubbled through liquid oxygen contained
in the inner tank. The ozone goes into solution and the oxygen
carrier gas passes through the heat exchanger to cool the incoming
gaseous mixture before being vented to the atmosphere. Continuation
of this process permits concentration of the ozone to any desired
value. The liquid level in the mixture tank is maintained by
bleeding liquid oxygen from the refrigerant jacket. After
unsuccessfully trying for several months to make the differential
manometer method work, the liquid level in the mixture tank and the
concentration of the mixture are both monitored currently by using
an ARF capacitance method based on the wide difference in the
dielectric constants of ozone and oxygen. Liquid level in the
refrigerant jacket is controlled by a thermister device which has
had operational difficulties. Temperatures of the mixture and
refrigerant are monitored to keep from inadvertent formation of the
two phase solutions at the higher concentrations above 25% ozone.
The refrigerant is kept somewhat above the liquid oxygen atmospheric
boiling temperature by pressurizing it to about eight pounds per
square inch using a back pressure regulator. Freon will also be
used to prevent the two phase formation and as an aid in stabilizing

CONFIDENTIAL

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the ozone. Experience in operating the system has shown the necessity for heating the out-gas from the mixture tank so the ozone is not recondensed by expansion through valve constrictions or by contact with gaseous oxygen below the ozone boiling temperature. Successful operation of the system depends on the proper temperature control to **prevent concentration of the mixtures by oxygen boil-off.**

The low pressure generation system is isolated from the rocket system for the test runs of the rocket motor and the mixture tank is pressurized to approximately 50 pounds above the pressure in the liquid oxygen tank. After the start has been negotiated on liquid oxygen the mixture tank main valve is opened, the additional pressure acts on an upstream check valve to cut off flow from the liquid oxygen tank. At the conclusion of the ozone mixture portion of the run the mixture main is closed and the liquid oxygen flow takes over again until shutdown.

Successfully dumping the remaining ozone mixture can be quite a problem. The need for detailed design, careful installation, and proper procedures is only too readily evidenced here by the number of detonations we have experienced. Our art, if any, lies in never having blown up the mixture tank.

One of the main component problems involves small static leaks and leakage past moving seals. Use of the teflon dispersion and careful testing has largely eliminated the problem of pipe thread leakage which was quite troublesome. Leakage past moving seals in valves and elsewhere in which the ozone escapes from inside the system and reliquifies on contact with gaseous oxygen or surfaces below its boiling point can be troublesome

The necessity for keeping the system sufficiently cold so the oxygen will not boil-off and concentrate the mixtures is paramount. This can be accomplished by the use of refined cryogenic techniques and procedures involving heavily insulated, vacuum-jacketed or refrigerated components, experienced installation methods and closely patterned procedures. The removal of the liquid sampling system resulted from our inability to handle these problems with the system as installed.

Although it has been possible to use or modify some existing **valves, e.g.; Annin 1520 and the Marotta PV20F, the need for a** specialized valve for ozone service became evident. Figure 30 shows the fluid actuated version of such a valve which is in final stages of development in both fluid actuated and manual **versions, the** Marotta PV32 and PV32A respectively. This valve has no body cavities or metal-to-metal contact. Provisions are being made for refrigerating the body and a servo control is under development.

Toxicity of ozone presents a serious problem that is not yet completely defined. Efforts to solve the problem by care in

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Installation and operation involving careful leakage tests, placing catalyst chambers on all vents, etc. do not allow sufficiently for the accidental eventuality which is always present in such research efforts. With increased concentration or length of exposure the **almost pleasant contact with ozone from natural causes or occasional** electric arcing is replaced by a strong ammonia-like smell and constriction of the nasal and throat passages sometimes accompanied by temporarily uncontrollable coughing. Gas masks with utility cannisters have been used successfully for short times.

Summarization of the results of operating the generation system show a considerable number of runs up to the 15% ozone mixtures. Generation of 5 to 10% mixtures is now routine while trouble continues to be experienced in dumping.the 15% mixtures. It is felt that the final difficulties with these mixtures are being solved and that we will soon be able to proceed to the 25% mixtures with some confidence of being able to show a completely acceptable system sometime thereafter.

Operation of the rocket system includes about 20 tests with up to 10% ozone mixtures most of which are sufficiently successful to be called routine. The two tests in the 10 to 15% concentration range were successful from rocket operation stand-points. No major difficulties with the 25% ozone mixtures from a rocket operation standpoint are anticipated. Some time may need to be spent in developing procedures for handling, and especially dumping, the 25% concentration mixtures.

Since the improvement in performance over liquid oxygen for 100% ozone is about 6 to 7-1/2 percent the evaluation of a rocket using 25% ozone depends on measurements at about the present limit of precision for the rocket field. It will be necessary to make steady state measurements of fuel and oxidizer flow, thrust and chamber pressure to better than 1/2 of 1 percent. With proper corrections and considerable calibration these are obtainable at our laboratory for fuel flow and thrust. The problem of measuring liquid oxygen and ozone mixture flow is being undertaken by attempting the precision calibration of a Potter turbine type flow-. meter using the measurement of flow rate from a completely self-contained system mounted on a scale.

Combustion chamber pressure is being measured by a further development of the Li-Liu high frequency response, water cooled, bonded strain column sens'ng element developed for our combustion instability research. Average steady state chamber pressure is measured by matching the impedance of a L & N Speedomax recording potentiometer and depending on its amplifier to average the fluctuations. The high frequency output of the pickup will be recorded on an Ampex tape recorder and used to evaluate effects of the ozone mixtures on combustion efficiency, level of fluctuations and stability limits.

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CONCLUSIONS

While the above presentation is primarily a summary of our experience with liquid ozone-oxygen mixtures, some attempt to make at least a preliminary evaluation is probably expected. In matter of fact, no such evaluation on our part can yet be recorded. We, at present, have a "conditioned optimism" with respect to the possibility of using the 25% ozone mixtures in rocket systems.

More work is needed on the fundamental character of the unstable behavior of ozone including the effect of sensitizing agents and thei, identification in kind and degree. A considerable part of such effort would seem to be instrumentation development.

Criteria need to be established for generation system design and components and installation methods developed. Cryogenic technique will probably always be a major factor in the generation, storage, transfer and disposal of liquid ozone and its mixtures.

More work is needed on the special requirements for the design of rocket systems and especially components. The primary problems surround the selection of suitable materials and their preparation for ozone service, the utilization of refined cryogenic techniques, the application of automatic controls and development of reliable instruments. A major problem which needs early attention is the pumping of the ozone mixtures.

It is expected that interesting and instructive results will emerge from the kinetic studies of ozone reactions and the effort to correlate them with results relating to performance and combustion from the rocket motor tests.

Further efforts to assess the toxicity problem and to develop monitors and protective devices are needed.

In the final analysis all of the factors must be applied in an objective manner against the payoff. The factors are so many and, as yet, largely untested that it seems premature to attempt any but the most preliminary evaluation of liquid ozone-oxygen mixtures as rocket oxidizers. However, the general possibilities seem sufficiently attractive to warrant continued active efforts.

CONFIDENTIAL

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CONFIDENTIAL

Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Ethyl Alcohol (95%) - Water (5%) (by wt) at 20 Atmospheres Chamber Pressure

FIGURE 1

FIGURE 2

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FIGURE 3

Theoretical Performance Calculations - Adiabatic Combustion Temperature, Average Molecular Weight and Average Specific Heat Ratio of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures & Ethyl Alcohol (95%) -Water (5%) (by weight) at 20 Atmospheres Chamber Pressure

FIGURE 4

FIGURE 5

Theoretical Performance Calculations - Adiabatic Combustion Temperature, Average Molecular Weight and Average Specific Heat Ratio of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures & Ethyl Alcohol (95%) -Water (5%) (by weight) at 60 Atmospheres Chamber Pressure

FIGURE 6

Theoretical Performance Calculations - Mole Fraction of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Ethyl Alcohol (95%) -Water (5%) (by weight) at 20 Atmospheres Chamber Pressure

FIGURE 7

FIGURE 8

FIGURE 9

Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Unsymmetrical Dimethyl Hydrazine at 20 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

NOTE: Based on oxidizer injection temperature of -183°C and fuel injection temperature of +25°C.

LEGEND:

① 100% Liquid Ozone
② 25% Ozone-75% Oxygen (by weight)
③ 100% Liquid Oxygen

FIGURE 10

CONFIDENTIAL

Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Unsymmetrical Dimethyl Hydrazine at 40 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

FIGURE 11

CONFIDENTIAL

Theoretical Performance Calculations – Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Unsymmetrical Dimethyl Hydrazine at 60 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

FIGURE 12

Theoretical Performance Calculations - Adiabatic Combustion Temperature, Average Molecular Weight and Average Specific Heat Ratio of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures & Unsymmetrical Dimethyl Hydrazine at 20 Atmospheres Chamber Pressure

FIGURE 13

CONFIDENTIAL

Theoretical Performance Calculations - Adiabatic Combustion Temperature, Average Molecular Weight and Average Specific Heat Ratio of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures & Unsymmetrical Dimethyl Hydrazine at 40 Atmospheres Chamber Pressure

NOTE: Based on oxidizer injection temperature of -183°C and fuel injection temperature of +25°C.

LEGEND:
① 100% Liquid Ozone
② 25% Ozone-75% Oxygen (by weight)
③ 100% Liquid Oxygen

FIGURE 14

CONFIDENTIAL

Theoretical Performance Calculations - Adiabatic Combustion Temperature, Average Molecular Weight and Average Specific Heat Ratio of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures & Unsymmetrical Dimethyl Hydrazine at 60 Atmospheres Chamber Pressure

FIGURE 15

172

FIGURE 16

Layton, Glassman, & Garvin

FIGURE 17

174

CONFIDENTIAL

FIGURE 18

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Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen at 20 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

FIGURE 19
CONFIDENTIAL
176

Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen at 40 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

FIGURE 20

Theoretical Performance Calculations - Effective Exhaust Velocity Vs Propellant Mixture
Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen
at 60 Atmospheres Chamber Pressure

Frozen Equilibrium   Sea Level Exhaust

FIGURE 21

FIGURE 22

FIGURE 23

FIGURE 24

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Theoretical Performance Calculations - Mole Fraction of Combustion Products vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen at 20 Atmospheres Chamber Pressure

FIGURE 25

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Theoretical Performance Calculations - Mole Fraction of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen at 40 Atmospheres Chamber Pressure

FIGURE 26

183

Theoretical Performance Calculations - Mole Fraction of Combustion Products Vs Propellant Mixture Ratio for Various Liquid Ozone-Oxygen Mixtures and Liquid Hydrogen at 60 Atmospheres Chamber Pressure

FIGURE 27

184

FIGURE 28

LIQUID OXYGEN SUPPLY SHED

VAPORIZER CABINET

OZONATOR SHED

CONTROL ROOM

FROM H2O SUPPLY

TO MIXTURE TANK
REFRIGERANT JACKET

FREON

Generation System and Rocket System Flow Diagram - Revision 2

re Generation System and Rocket System

LIQUID
OXYGEN

FUEL

Ozone Mixture Cell

and Rocket System Flow Diagram - Revision 2

FIGURE 29

(Face blank page 186)

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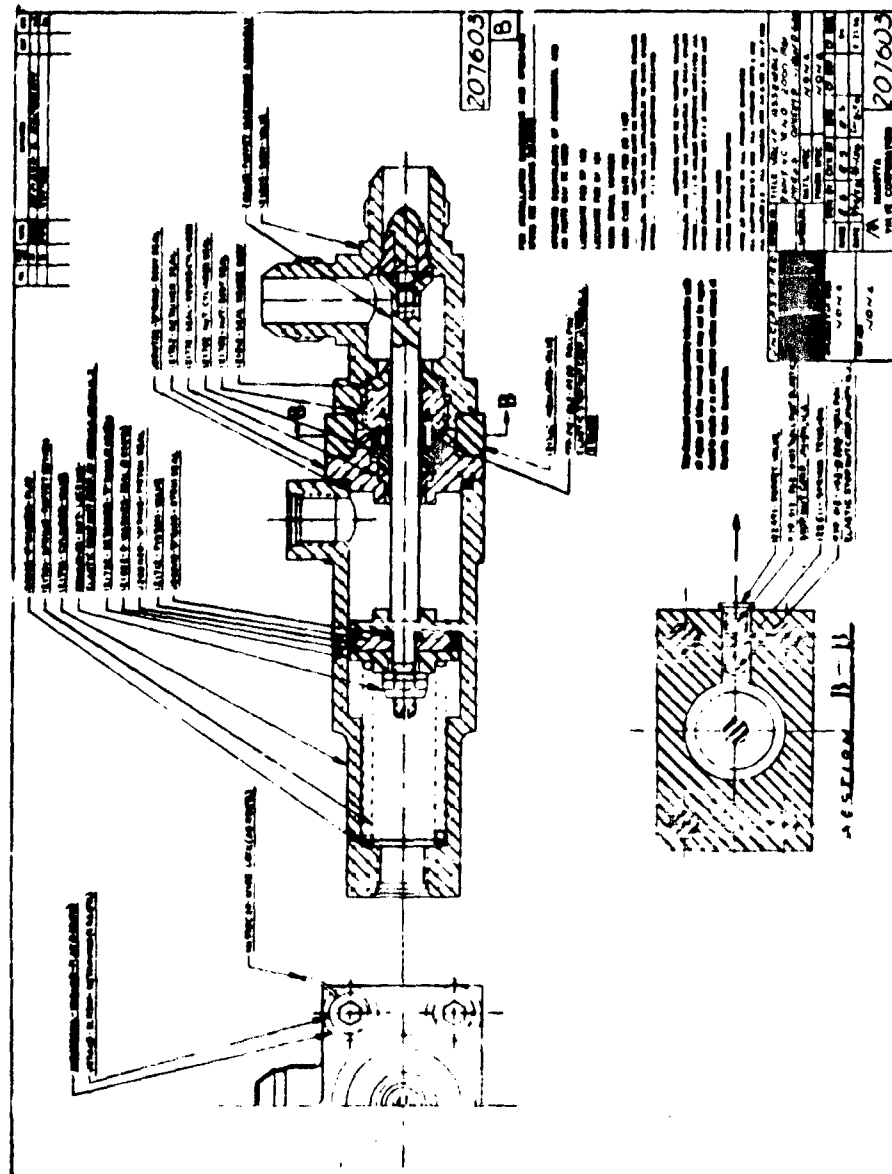
Liquid Ozone (25%)-Oxygen (75%) Mixture Valve-Harotte PV32

FIGURE 30

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HIGH TEMPERATURE RESEARCH AT TEMPLE

A. V. Grosse, C. S. Stokes, and W. L. Doyle
The Research Institute of Temple University
Philadelphia, Pennsylvania

I would like to present some of the results that we have obtained at Temple in the general field of high temperature research. We have been in this field for the last nine years and, obviously, at this meeting we cannot go into details and discuss all the various phases of the work but, at least, I would like to give you a brief outline of our research.

Our work was supported originally by the Office of Naval Research and later by Army Ordnance, and particularly by Redstone Arsenal. We have also been sponsored by the U. S. Air Force Office of Scientific Research.

Primarily we were interested in producing high temperatures by chemical means. We were then interested in studying various chemical-physical phenomena at these high temperatures. The field is wide open and from the various topics that I will discuss with you, I think you will agree that the surface of the whole field of high temperature research has only been scratched.

In order to produce high temperatures by chemical means, one must have a highly exothermic chemical reaction and the products of combustion should be stable. This requirement is met by the simple metals -- magnesium, aluminum, and zirconium -- which have become more readily available in recent years.

Our Institute used a very simple setup that originally developed from some experiments that were carried out with the unforgettable Enrico Fermi at Columbia University in the early days of the Manhattan Project.

The apparatus consists, essentially, of a hollow sphere made out of the oxide of the metal that is being combusted and the metal and oxygen are fed through side ports. The top is water-cooled so we can see what is going on.

I would like to emphasize that there is a tremendous difference in the behavior of the combustion of these three simple metals; magnesium, aluminum, and zirconium. They all produce high temperatures: magnesium, atmospheric pressure, adiabatic temperature equals 3000°K; aluminum, 3800°K; and zirconium, 4900°K.

The physical properties of both the metals and particularly the oxides, are different and that characterizes the phenomenon one observes. Magnesium boils at 1100°C and if it is fed into a furnace of a simple type, most of the magnesium boils out and burns in a big flash outside.

In the case of aluminum we have an interesting phenomenon that I would like to describe. As an aluminum rod or wire is fed into the pot, we get the so-called "skating sun." The oxygen stream comes from the top and the aluminum boils and burns in the atmosphere of oxygen. A similar situation occurs when a drop of water hits a red-hot plate where the drop or puddle of water boils on the surface of the solid material. In this case, it actually skates over the surface of the liquid aluminum oxide as a boiling pancake of metallic aluminum. The boiling vapors then meet the stream of oxygen about 1 mm above the surface of the liquid and there produce a very brilliant, radiant disc-like object which looks like the sun. So the whole thing is described as the "skating sun" because the liquid aluminum can move back and forth over the surface of the liquid. If it is adjusted to burn in the middle, it will keep reasonably constant.

One interesting possibility of producing high temperatures in substantial volume very easily, is to rotate this "skating sun" over the surface of a cylinder. To illustrate: if you have a fork on one side and a stuffing box on the other in which to feed the metal either in the form of rod, pipe, or wire with the oxygen, and rotate the whole apparatus, you will have a chemical reactor. We call it a centrifugal reactor where the whole inner surface of the cylinder is the "skating sun." Here you attain an overall temperature of about 3800°K at 1 atm and the aluminum oxide boils out at a rate corresponding to the feeding of the aluminum, either one-half or one lb/min.

In a similar operation with a magnesium feed the color of the flame is different. It is more brilliant, but we also have here another phenomenon which is not normal. Some of the liquid magnesium oxide, melting at about 3100°K, is spilled out in a "squirt." If you really want to have a hot shower, this is it!

Because zirconium metal has practically no vapor pressure at 3000°K and also because the product of combustion, zirconium dioxide, has no vapor pressure, a completely different set of phenomena occurs when this metal is used. When the metal is burned it becomes highly radiant at 2000° or 3000°K but burns in the liquid state. That is something that will have to be studied much more fully. Diffusion of oxygen occurs through the liquid which at these temperatures of the

order of 3000°K is very rapid, and the whole mass seems to burn right through the liquid. I should like to emphasize that with a metal like magnesium you have one set of phenomena, which essentially burns like a vapor. Aluminum, on the other hand, is a sort of intermediate stage which shows a "skating Sun," whereas zirconium burns as a liquid.

Another method for producing high temperatures is the use of a powdered metal oxygen torch. Because the products of combustion are highly refractory and at a high temperature and therefore condense on any surface, releasing their heats of vaporization, the flame of the torch will have a very effective heat transfer mechanism and will melt through any material; e.g., reinforced concrete, granite, etc.

The so-called "dog" of the steel industry cannot be cut by any other means. A "dog" is composed of bricks, concrete, iron, etc., so it cannot be touched by oxy-acetylene or by a pneumatic hammer, but it can be cut by an oxy-aluminum torch.

If we look at the molecules that are present in the sun -- and there are only about ten -- we will find the most thermally stable molecules are carbon monoxide and nitrogen, so any reaction that will produce these as products of combustion, will produce a very high temperature providing the reaction is highly endothermic. We have been combusting cyanogen, a very nice material to handle although poisonous. It is not recommended that it be inhaled. We have been living with it for the last seven years or so and have been using it. In combusting cyanogen and oxygen, we can get a temperature of 4800°K. I will just mention briefly that we measure these temperatures by comparing these flames directly with the sun, using the well-known line-reversal method.

In addition to cyanogen we have discovered recently that there are some other compounds which will produce even higher temperatures. These are the so-called carbon subnitrides which are essentially the dicyano-polyacetylenes. The first member, dicyano-acetylene, has properties similar to benzene, melts at about +20°C, and has a negative heat of formation of +140 Kcal/mol. It is quite a potent compound when combusted with oxygen. We found that we could bubble oxygen through the compound and burn it in a premixed flame. This flame produces a temperature of 5150°K at 1 atm pressure and at higher pressures as would be used in rocket motors, 5750°K.

Instead of using endothermic fuels, it is obvious, of course, that one could use endothermic oxidizers. The best thing to use, instead of oxygen is the molecule O_3 (ozone). I will describe a few of our experiments with ozone, for there is much interest in that material by researchers in the liquid propellant field.

Ozone has the advantage in that it has a negative heat of formation of 33 Kcal/mol. It has a high density and a higher boiling

point than oxygen, but one has to learn how to handle it in order to avoid detonations.

The first thing we were interested in doing was to burn pure ozone. The decomposition flame of O_3 to O_2 has a flame temperature of about 2700°K and one would expect that it would produce a visible flame. We have been able to burn 100% ozone, starting first with dilute mixtures. The pure ozone flame is not very impressive because the oxygen molecule radiates very little light in the visible. It is just a pale blue flame with a characteristic pink cast. It can be seen above the range of about 70% ozone in oxygen. Below that range, it is not visible to the naked eye unless one is experienced, but can be detected on a schlieren apparatus.

Temple does not have the reputation that Princeton has to uphold in the field of research because we are newcomers. Our apparatus, for that reason, is extremely simple! The whole apparatus is just a glass gas-holder with one stopcock and the ozone mixture is pressed out with water. The point is, we cannot get into much trouble! We used water for our gas-holder, gas-expelling mixture. We had an ice trap that took out the water vapors. When referring to pure ozone, I mean pure ozone and not diluted.

By the techniques of the schlieren method one can measure burning velocities which are not high at all. Pure 100% ozone at atmospheric pressure and room temperature burns at a velocity of 475 cm/sec. Mixtures of 50% or 25% burn with lower velocities and the low ignition limit is at 17 mol % O_3, the burning velocity being about 10-15 cm.

The ozone flame is also of particular interest because it is the simplest flame imaginable. You merely have O_3 molecules as the fuel oxidizer mixture, and only O_2 molecules as the product of combustion, the only possible intermediates being oxygen atoms. In recent years, J. O. Hirschfelder of Wisconsin, T. von Karman of California, and R. Sandri of Westinghouse, have developed a theory of laminar flame propagation. The simplest decomposition flames are those of ozone and hydrazine. The above mentioned scientists checked the theoretical calculations against the results of Lewis and von Elbe who exploded ozone and oxygen 15 years earlier, but only went up to the range of 50% ozone. We asked these gentlemen to calculate and apply their theories to the 100% range. I was very much surprised and flattered when Dr. von Karman called me from California and said he would be glad to do it. He presented the theoretical calculations at the High Temperature Symposium held at Berkeley, California, June 25-27, 1956. These were in agreement with the experimental values.

Carbon monoxide ignites spontaneously with ozone, whereas cyanogen does not. Recently, we have been able to mix 100% pure ozone with hydrogen, cyanogen, and methane. We allowed the cyanogen-oxygen mixture to stand at room temperature for substantial periods of time with no noticeable reaction occurring.

We have just recently finished determining the burning velocities of the ozone-hydrogen system. You have read in textbooks that if you take two volumes of hydrogen and one volume of oxygen, you get water. That is no longer true if you take the oxygen in the form of ozone, for then you will have to take three volumes of hydrogen and one of ozone. You then get the water formed in the same amounts. That is a complicated way to produce water. This can be accomplished without detonations.

We have operated these flames at dry ice temperatures at -77°C at the stoichiometric point. The burning velocities are 620 cm/sec for the oxygen and 1680 cm/sec for the ozone. Thus it can be seen that the hydrogen-ozone mixture burns two and one half times faster than the oxygen system, both leading to water as products of combustion. The kinetics of the whole reaction rate of combustion are very markedly increased by ozone as compared with oxygen.

We have also combusted hydrogen and fluorine premixed flames which are still faster than the ozone flame and give interesting possibilities for a study of very fast flames running at a rate of about 20 to 25 meters per second.

We found that liquid ozone and liquid fluorine can be mixed in any proportion which gives the possibility of studying ozone-fluorine mixtures. We also know that there are compounds of oxygen and fluorine. A well known one is OF_2, which is a stable gas. Another is O_2F_2 which we have been studying recently. This is an orange-red liquid with a boiling point of 57°C.

An interesting point is that there is a Japanese paper, dated about twenty years back, on the compound O_3F_2 which we have been handling recently and prefer to call ozone-fluoride. For some reason this Japanese work which was published before Pearl Harbor was considered unreliable. None of our reliable textbooks on chemistry make any reference to these two Japanese papers. The reason for that may be that the Japanese workers, Aoyama and Sakuraba, did not determine the composition of this compound by standard chemical analysis but just determined the ratio of oxygen to fluorine and found it varies between one and one and one half. In those cases where it was one and one half, they explained they had the pure O_3F_2 compound. In the other case, they had O_2F_2. I do not have time to go into details except to tell you we have distilled and isolated pure O_3F_2. It is a blood red liquid, much darker in color than the O_2F_2 and is stable at liquid oxygen temperatures. We have determined the formula. It is O_3F_2 and we are just beginning to determine its heat of formation which is most important. We have recently determined the heat of formation of O_2F_2 as -50 Kcal and O_3F_2 is likely to be -15 Kcal.

We have set up the hottest rocket motor which we believe exists in this country by combusting cyanogen and oxygen. This has been accomplished by Mr. William L. Doyle, director of our high temperature establishment.

COMPARISON OF LOX/KEROSENE, LOX/HYDRAZINE, AND
FLUORINE/HYDRAZINE AS PROPELLANTS FOR LONG-RANGE ROCKETS

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INTRODUCTION

During a theoretical study of future propulsion systems of
rockets above 1000 N. mile range, the choice was narrowed to very few
propellants. The following criteria were applied in this selection:

1) a sizable production of the propellant must exist, suffi-
cient for immediate start of developmental testing,

2) performance must appreciably exceed that of the present
propellant, LOX-Jet fuel. The more difficult appears to
be development and handling of the new propellant, the
greater must be the gain in performance.

3) there must be some experimental proof of the fitness of
the propellant.

PRELIMINARY COMPARISON BASED ON "CAPACITY FACTOR"

Judging rocket propellants by their specific impulse has
been shown to be totally inadequate. The only decisive parameter is
the range obtained for a given payload with respect to mass of pro-
pellant and of structure expended and with respect to the volume of
the rocket.

Three parameters are readily apparent to chiefly determine
the range. They appear in this form of the ideal cut-off velocity

$$U_{id} = I_{sp} \, g_c \, \log \, \mathrm{nat} \, \underbrace{(1 / D \, \theta)}_{\text{mass ratio}} \qquad \qquad [1]$$

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where: U_{id} . . . velocity of rocket at cut-off for flight in vacuum, free of gravity

I_{sp} . . . specific impulse

g_c . . . standard acceleration of gravity as mass-force conversion factor

D . . . propellant density

θ . . . "capacity factor", tank volume per unit cut-off mass (specific tank volume)

While D is a propellant property like I_{sp}, the parameter θ (speak: theta) is a design parameter of the rocket, expressing the achievement of light-weight design: a larger θ means more tank volume obtained for a given cut-off mass. Note that the payload is also contained in this parameter as cut-off mass, and so is residual propellant.

For a given payload the parameter θ has a tendency to grow with longer ranges. From actual rocket designs or from some design studies, one will be able, at a given state of art, to assign some value of θ characteristic of a certain payload-range mission.

Equation [1] is easily expanded to account for deceleration by gravity and to yield the vertical ascent range. Simplication is obtained by the following assumptions:

(a) constant thrust during propelled period,

(b) thrust to starting weight ratio ≈ 2 (≈ initial acceleration ≈ g_c),

(c) no air drag,

(d) constant gravity (as at surface of earth).

The range of vertical ascent follows:

$$H \approx \frac{g_c}{2} I_{sp}^2 \left[\frac{D\theta}{1 + D\theta} + \ln^2 (1 + D\theta) - \ln (1 + D\theta) \right] \quad [2]$$

Most conveniently, propellants are compared at constant capacity factor. Choosing θ = 7 lit/kg as typical for a rocket of about 1500 N. Mile range, the relative range of a number of propellants are compared in Table 1.

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TABLE 1

Relative Ascent Altitude H from Equ. [2]
for θ = 7 lit/kg

F_2-N_2H_4	1.92
F_2-NH_3	1.61
F_2-O_2-JP	1.58
ClF_3-N_2H_4	1.41
O_2-N_2H_4	1.22
H_2O_2-N_2H_4	1.22
90% H_2O_2-N_2H_4	0.96
O_2-JP	1.00

From this group, 4 propellants were selected for closer
scrutiny:

1) O_2-JP as reference standard.

2) O_2-N_2H_4 as a propellant of some improvement, but moderate
   developmental difficulties, since the oxidizer is being
   retained.

3) H_2O_2-N_2H_4 as a propellant of "storable" type, meaning to be
   liquid at normal temperature. 90% concentration was prefer-
   red to the anhydrous H_2O_2, because of the lack of motor tests
   with the latter.

4) F_2-N_2H_4 as top performer. The intermediate fluorine combi-
   nations were disregarded with the reasoning that the
   developmental and handling difficulties with fluorine (and
   its compounds) could only be justified by top performance.

COMPARISON BASED ON MISSILE DESIGN OF VARIABLE LENGTH

The basis of comparison was a 1500 N. Mile rocket equipped
with a 200 K engine with LOX/Jet fuel as propellant.

TABLE 2

Description of Reference Rocket
1500 N. Mile, LOX/JP

Cut-off Mass (pounds)

Nose Section (payload, structure, instr., etc)   4800

Center Section (propellant tanks)   2000 (variable)

Tail Section (engine, structure, auxiliary)   4300

Residual Propellant at Cut-off   1300

Cut-off Mass   12,400 (variable)

Overall Length (feet)   55 (variable)

Caliber (cylindrical body) (inch)   104

Thrust (lbF), sea level   200,000

     Of the design parameters listed in Table 2, the ones designated "variable" were allowed to vary; the others were held constant.

     The size of the rocket was increased by merely extending the length of its center section.

     The increment of cut-off mass was assumed to be 50 lbM per foot length, composed of 43 lbM metal and 7 lbM pressurizing gas.

     There could be some doubt on the validity of the assumption of a constant engine mass. It was justified by an estimation that the design changes imposed by changing propellants would amount to changes of engine mass of only ±10%. Since the engine mass constitutes about 20% of the total cut-off mass of the standard rocket, the propellant change may impose only ±2% change of cut-off mass; this, in turn, would cause a variation of range by about ±2%, which is well within the accuracy of the entire estimation.

RANGE CALCULATION

     The length was varied in steps of 5 feet, the consequent changes of mass ratio, burning time, cut-off velocity, etc., and finally range calculated. A closed equation had been derived rendering the maximum range with consideration for gravity and air drag at constant mass flow rate.

Koelle & Tschinkel

Thrust variation with altitude is accounted for by use of an average thrust as follows:

$$F_{av.} = F_{sea\ level} + 0.8\ (F_{vac.} - F_{sea\ level}) \qquad [3]$$

A set of typical intermediate data is given in the following table:

TABLE 3
Example of Calculated Data
Propellant, LOX/JP

Missile Length	ft	55	60	65	70
Cut-off Mass	lbM	12400	12650	12900	13150
Increment	lbM		250	250	250
Propellant Mass	lbM	86705	105630	124555	143480
Increment	lbM		18925	18925	18925
Take-off Mass	lbM	99120	118295	137470	156645
Increment	lbM		19175	19175	19175
Initial Acceleration	g_0	1.0176	0.6907	0.4550	0.2768
Decrement	g_0		0.321	0.235	0.178
Mass Ratio	—	7.984	9.340	10.644	11.898
Increment	—		1.356	1.304	1.254
Burning Time	sec	111	135	159	183
Mass Flow Rate	lbM/sec	794	=	=	=
Exhaust Velocity	m/sec	2765	=	=	=
Ideal Cut-off Veloc.	m/sec	5744	6178	6539	6847
Veloc. Decrease due to Gravity	m/sec	888	1080	1272	1464
Veloc. Decrease due to Drag	m/sec	260	200	167	153
Cut-off Velocity	m/sec	4596	4818	5100	5230
Range	N.Mi.	1508	1800	2020	2180

PROPELLANT PERFORMANCE COMPARISON

The result of these calculations for the chosen four propellants is shown in Figure 1.

Inspection of this graph leads to the following conclusions:

(a) 90% H_2O_2/N_2H_4 does not improve the range performance. Its only merits vs. LOX would lie in the "storability" of the oxidizer, meaning that it is a liquid at normal temperature.

(b) Accepting a take-off acceleration of 0.2 g as limit of feasibility, it can be seen that the limits of feasible range are, for a single stage rocket of the given design:

TABLE 4

Feasible Range (0.2 g take-off acceleration) of
Single Stage Rockets

	N. Mi.	Rel.
LOX-JP	2250	1.0
90% H_2O_2/N_2H_4	2050	0.91
LOX-N_2H_4	2750	1.22
F_2/N_2H_4	4200	1.87

F_2/N_2H_4 would allow to build a missile of near ICBM range (5000 N.Mi.) in a single stage, and this at a missile length only 10 feet longer than a LOX-JP IRBM missile (1500 N.Mi.).

(c) Comparing missile length at given range leads to the following result:

TABLE 5

Missile Length vs. Range, ft. (relative)

Range	LOX-JP	90% H_2O_2/N_2H_4	LOX/N_2H_4	F_2/N_2H_4
1500	55 (1.00)	55 (1.00)	52 (0.95)	45 (0.82)
2000	64.5 (1.00)	66 (1.025)	58 (0.90)	48 (0.75)
2500	out	out	66 (1.00)	50.5 (0.765)

In Figure 2, the take-off mass is presented as a function of range for the four propellants, with lines of constant missile length.

It can be seen that the peroxide-hydrazine rocket would be heavier than the LOX-JP rocket at a given range, whereas, the other two propellants yield significantly lighter rockets. At the limit

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of the LOX-JP rocket (2250 N.Mi.), the take-off masses compare as follows:

TABLE 6

Take-off Mass at 2250 N. Mile Range

	lbM	Relative
LOX/JP	165,000	1.00
90% H_2O_2/N_2H_4	(not feasible)	
LOX/N_2H_4	122,000	0.74
F_2/N_2H_4	85,000	0.515

In the foregoing calculations, propellant performance parameters were assumed as follows:

TABLE 7

Propellant Performance Parameters
800 psi Chamber Pressure

	O/F, Mass Ratio	Nominal I_{sp} Sea Level, (sec)	I_{sp} Vacuum (sec)	I_{sp} Average (sec)	Prop. bulk Spec. Grav.
LOX-JP	2.25	252	289	282	1.008
90 H_2O_2-N_2H_4	1.70	242	277	270	1.214
LOX-N_2H_4	0.835	271	311	303	1.060
F_2-N_2H_4	2.0	308	353	344	1.300

COMPARISON OF CALCULATED RANGES WITH VERTICAL ASCENT DATA (Equ. 2)

Under the assumption of this study, missile length (L) can be directly converted into θ-values.

By taking the cut-off mass of the 55 ft LOX-JP missile (see Table 2) as base value (12,400 lbM), the mass increment (50 lbM per ft), the base propellant volume (39,050 lit), and the volume increment (1694 lit per ft), the conversion of missile length into capacity factor is found to be nearly linear:

$$\theta = 6.93 + 0.259 \ (L-55) \qquad [4]$$

θ and L-scales are superimposed on Figure 1. Figure 3 shows relative ascent values and relative range values on same graph as function of

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both θ and L. It can be seen that the relative rating of the ascent values for the various propellants comes near the rating of the more accurate range calculation. The two curves seem to come nearer with larger missiles.

Curve IIA for 100% H_2O_2/N_2H_4 was inserted to show that its performance comes very near to the one of LOX/N_2H_4.

On the whole, one may say that the ascent method spaces propellants adequately if they are much different, but may not be representative for propellants of little different performance.
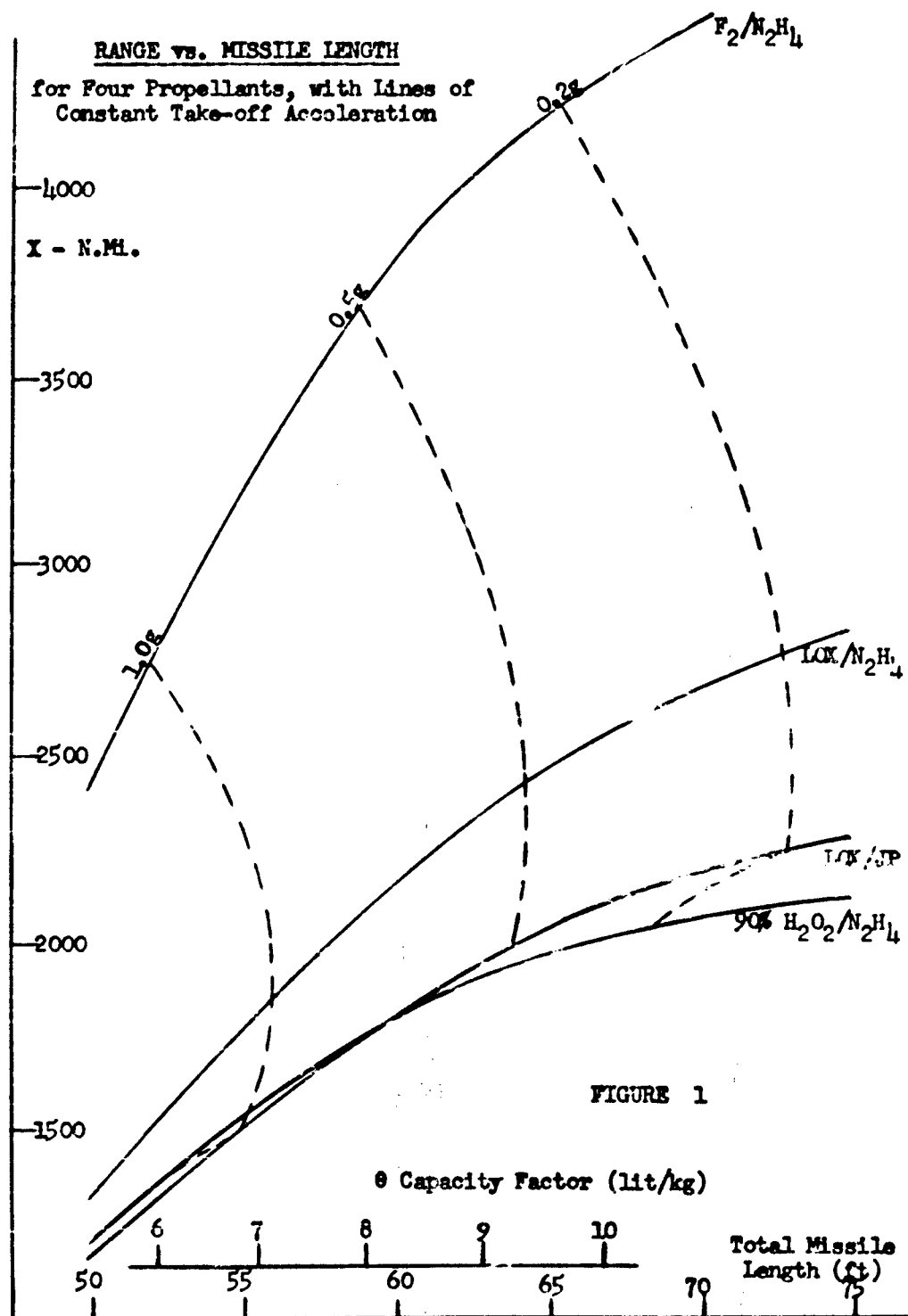
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RANGE vs. MISSILE LENGTH

for Four Propellants, with Lines of
Constant Take-off Acceleration

FIGURE 1

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FIGURE 2

TAKE-OFF MASS vs. RANGE
for Four Propellants
with lines of Constant Length

Range - N. Mi.

RELATIVE RANGE vs. MISSILE LENGTH (solid line), RELATIVE ASCENT ALTITUDE vs. CAPACITY FACTOR (dashed line) for Four Propellants (Reference: LOX/JP)

FIGURE 3

Legend:

——————— X/X_I vs. L

- - - - - H/H_I vs. θ

I — LOX/JP

II — 90% H_2O_2/N_2H_4

II A — 100% H_2O_2/N_2H_4

III — LOX/N_2H_4

IV — LF$_2$/N$_2H_4$

Missile Length - L

θ (lit/kg)
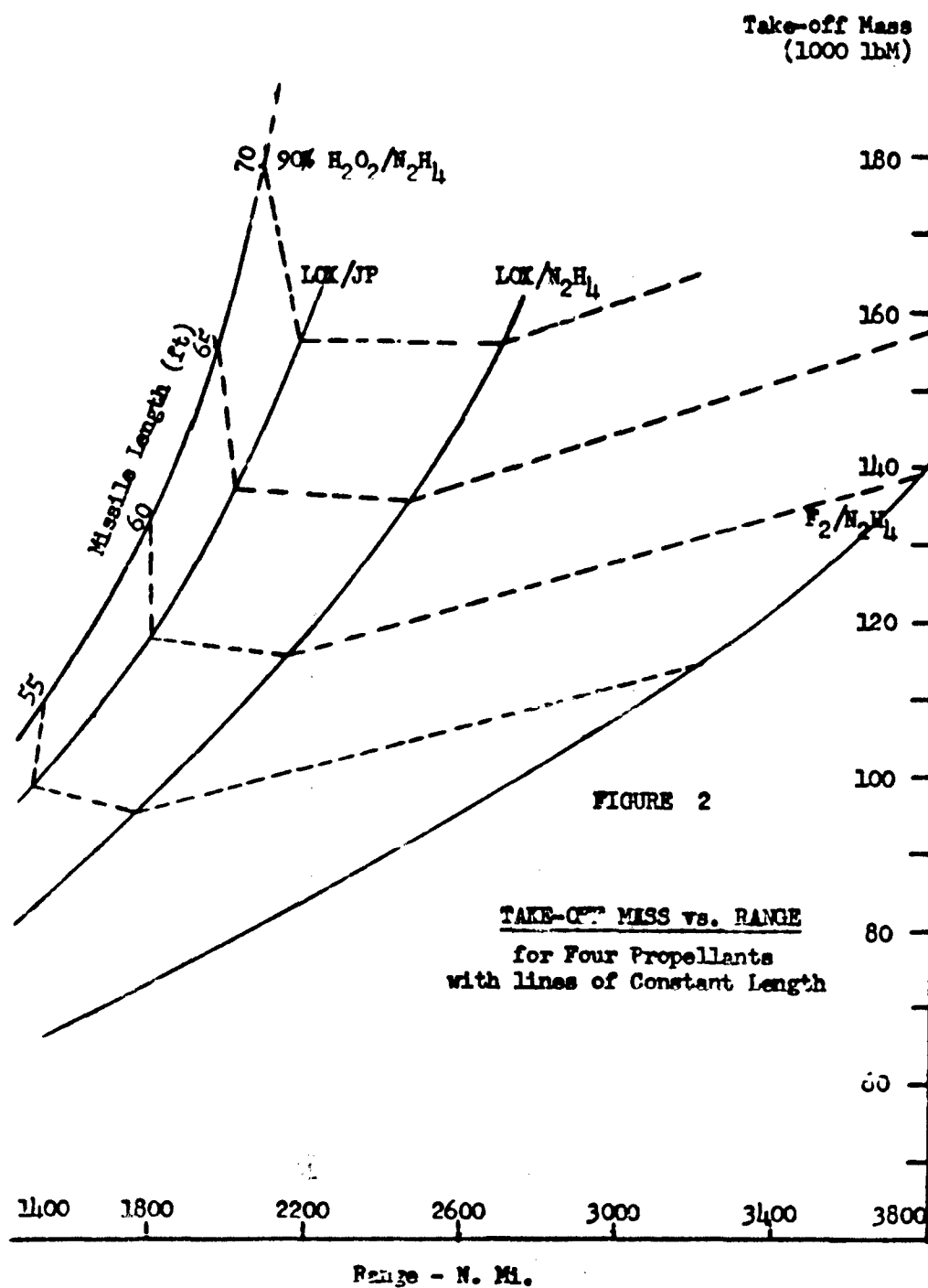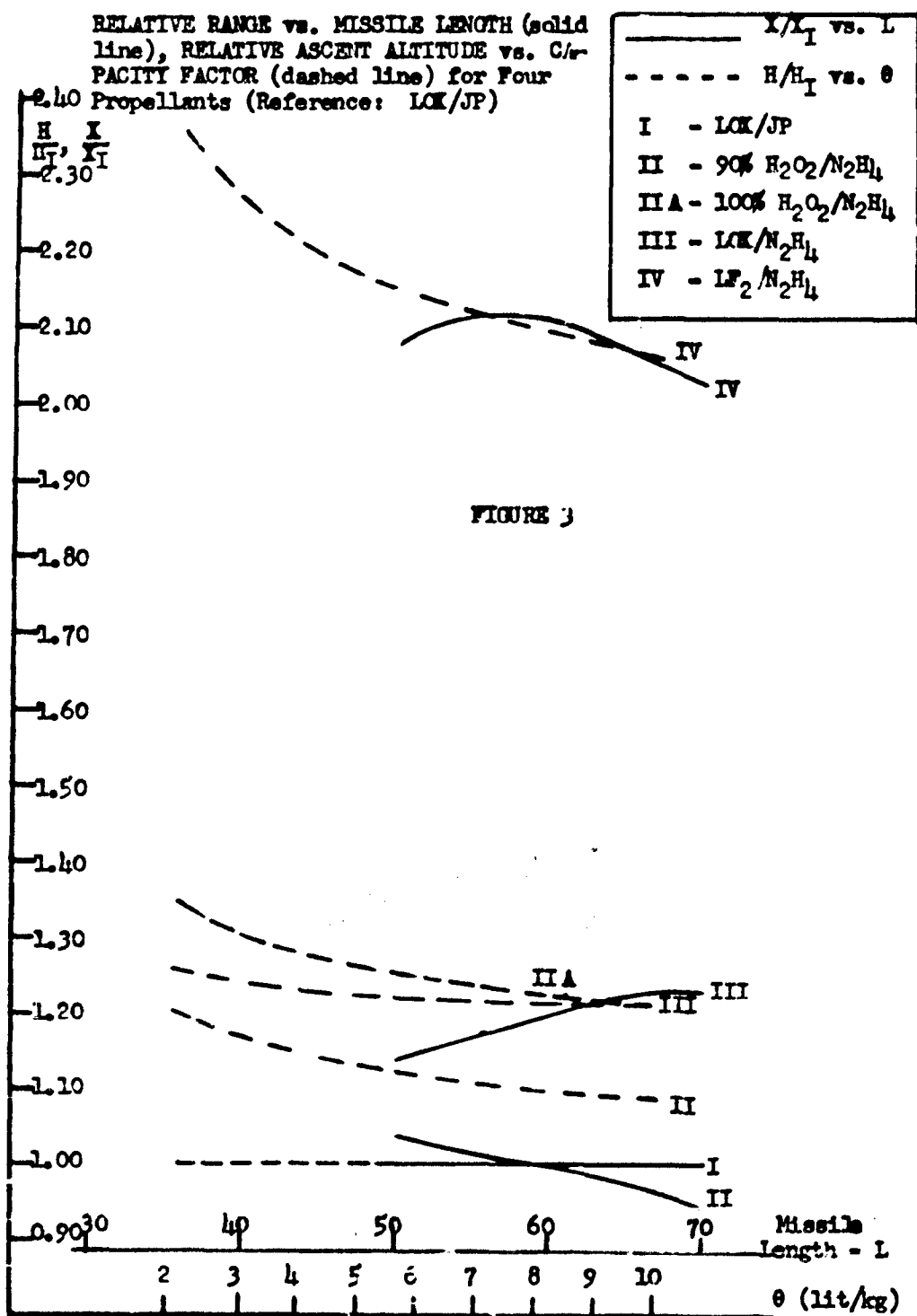
The following papers were read by title only at the symposium and were not received in time to be included with the preprints (Volume 2, PFL 212/13):

ACETYLENIC COMPOUNDS AS RAM- AND TURBO-ROCKET FUELS

John Happel and Charles J. Marsel
Department of Chemical Engineering
New York University

Acknowledgment

Acetylenic Compounds as Ram- and Turbo-Rocket Fuels

The jet propulsion devices known as ram- and turbo-rockets have been the objects of considerable research. In the ram rocket a fuel is first decomposed as a monopropellant in a rocket motor, and the exhaust products from this decomposition are burned in an air breathing device such as a ram jet. The principal advantage of this combination is that it has substantially higher thrusts than a simple ram jet motor at the low Mach umbers which correspond to launching velocities; a simple ram jet motor does not develop a positive thrust below a Mach number of 0.4.

In addition to fuel characteristics, the performance of a ram rocket is dependent upon a number of other factors; these include: a) altitude of operation; b) speed of launching; c.) maximum desired flight speed; d) desired range of operation; e) geometrical configuration of the ram rocket motor. Calculations which were made in these laboratories, indicate that different fuel characteristics will be important depending upon which of these parameters is being considered. For instance, a high monopropellant specific impulse will be conducive to a high thrust on launching. For a fixed size of ram jet air inlet, high launching velocities are favored by operation on the fuel rich side, but at the expense of lower performance at higher speeds. When the device is operating at speeds approaching a Mach number equal to one (1), the fuel specific impulse (specific thrust per pound of fuel in an air breathing device) assumes major importance (2, 3).

A study by Marquardt Aircraft Co. (4) illustrates some of the additional advantages of the rocket ramjet engine. Methylacetylene was considered as the fuel in this study, but it is believed that similar considerations would apply to this type of equipment using other acetylenic compounds as fuels. It was pointed out that under cruising conditions a ram jet initially brought up to speed by a rocket booster cannot develop as high a thrust for short periods of time as can be obtained in a ram rocket by simply increasing fuel flow. Another advantage is the ability of a ram rocket engine to remain ignited even under conditions of high angles of attack because of the pilot action of the rockets.

In a report on the air-turborocket cycle Eldridge (5) states: "This shows clearly the advantage of using primary fuels w th high heating values. Thus, development of practically useable fuels of the acetylenic type will provide the basis for a significant performance improvement."

The properties of a number of acetylenic compounds which may be of interest as ram and turborocket fuels are described below.

It is apparent that in these systems it is desirable to employ fuels which have relatively high monopropellant specific impulse values and which give rise to exhaust products possessing high heats of combustion with air. Methylacetylene (propyne) offers considerable merit as a fuel for this application. However, it has the disadvantage of having a high vapor pressure and a low density, and thus the weight of the storage vessel required per unit weight of propellant detracts from the advantage of its high specific impulse. In addition, there is some indication that there may be difficulty in obtaining high efficiency as compared to theoretical performance, and part of this difficulty may arise from the decomposition and combustion characteristics of methylacetylene. Other acetylenic compounds have lower vapor pressures and, in some cases, decompose more readily. These acetylenic compounds might be considered for use either alone or in blends containing methylacetylene.

Since acetylenic compounds are of considerable merit as ram- and turbo-rocket fuels, and since ethylene oxide is also of use in such applications, it appeared that it might be advantageous to utilize the energies of the triple bond and the strained three-membered epoxide ring by incorporating the two groups within a single molecule. Some of the more recent work at the N.Y.U. Laboratories has involved a detailed study of the preparations of acetylenic epoxides. As a result, a convenient synthesis of 2-methyl-1,2-epoxy-3-butyne has been developed. This compound is a liquid of relatively high density and is quite stable.

The structures and densities of a number of compounds which may be of interest as ram- or turbo-rocket fuels are listed in Table I. The theoretical performances as monopropellants have been calcu-

Table I

Names, Structures and Densities of Compounds which are of Interest as Ram- or Turbo-Rocket Fuels

COMPOUND	STRUCTURE	DENSITY (g/cc)	(lbs/ft³)
acetylene	H-C≡C-H	.5208	38.76 at -83.5°C
methylacetylene	H-C≡C-CH3	.6711	41.90 at -23.2°C
1,5-hexadiyne	H-C≡C-CH2-CH2-C≡CH	.801	50.00 at 20°C
1,6-heptadiyne	H-C≡C-CH2-CH2-CH2-C≡CH	.805	50.26 at 20°C
1,7-octadiyne	H-C≡C-CH2-CH2-CH2-CH2-C≡CH	.817	51.01 at 20°C
methylvinylacetylene	CH2=C - C≡CH / CH3	.680	42.45 at 20°C
methyldivinylacetylene	CH2=C - C≡C-C=CH2 / CH2	.781	48.76 at 20°C
cyclopropylacetylene	CH2 / CH-C≡C-H / CH2	.773	48.26 at 20°C
cyclopropylvinylacetylene	CH2 / C-C - C≡CH / CH2	.824	51.44 at 20°C
ethylene oxide	CH2 - O - CH2	.871	54.38 at 25°C and 1.441 atm.
epoxybutyne	CH2 / CH-C≡C-H	.945	59.00 at 20°C
1,2-epoxyhexen-5-yne-3	CH2 / CH-C≡C-C=CH2	-	57.44 at 20°C
2-methyl-1,2-epoxyhexene-5- yne-3	C - C≡C .C=CH2 / CH3	.920	57.44 at 20°C
methylepoxybutyne	O / CH2 / C - C≡CH / CH3	.894	55.81 at 20°C
dipropargyl amine	H-C≡C-CH2-N-CH2-C≡CH / H	.901	56.25 at 20°C
dipropargyl ether	H-C≡C-CH2-O-CH2-C≡CH	.924	57.69 at 20°C
JP-4	C₁₂H₂₆	.750	46.82 at 20°C

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lated for these compounds, and these data are summarized in Table II.
The adiabatic flame temperatures of the monopropellants have been
calculated and are included in Table II. In any missile application,
it is important to know the energy (thrust) that can be derived from
a given volume of fuel. A reasonable estimate of the effect of
density can be obtained from the product of the density and the mono-
propellant specific impulse value. These values have been calcula-
ted and are listed in Table II.

Included in Table II for purposes of comparison, are simi-
lar data for ethylene oxide, a conventional monopropellant. From
the data listed in Table II, it can be seen that many of the acetyl-
enic compounds have monopropellant specific impulse values that are
higher than that of ethylene oxide.

If those values which correspond to the products of the
monopropellant specific impulses and densities (density impulses)
are examined, some appreciation may be gained of the relatively high
thrusts that can be obtained from given volumes of the listed com-
pounds. It must also be remembered that the value of 129.3 for
methylacetylene is somewhat high because it was calculated using the
density of methylacetylene at -24.2°C. Of the compounds listed, only
methylvinylacetylene and methyldivinylacetylene are not as favorable
as methylacetylene, but even in these cases this could be outweighed
by the fact that methylacetylene boils at -9.4°F at atmospheric pres-
sure, and the other compounds boil at 92.8 and 225.9°F respectively.
In any consideration of this type, it is desirable that a fuel have
a high monopropellant specific impulse and a relatively high density.
It is interesting that dipropargyl ether has a high monopropellant
specific impulse, and also one of the highest densities of the com-
pounds listed. The value of 170.8 is indeed one of the highest den-
sity impulses listed and is 33% greater than the corresponding value
for methylacetylene. It is evident that the relatively high densi-
ties of the acetylenic compounds that contain either oxygen or nitro-
gen cause these compounds to be of interest in the current program.

The value of any ram-rocket or turbo-rocket fuel is de-
termined not only by its thrust derived as a monopropellant, but
also by the thrust derived by the combustion of the monopropellant
decomposition products with air. An accurate evaluation of any fuel
therefore requires the additional consideration of the material as a
fuel with air, and necessitates taking a number of other variables
into consideration.

An estimate can be made of the relative performances of
various fuels from a calculated value called the fuel specific
impulse (3).

Fuel specific impulse values of a number of acetylenic
compounds have been calculated and are listed in Table III along with
the values of the air to fuel ratios at stoichiometric combustion.

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Table II

Theoretical Performances as Monopropellants of Various Compounds
Which Are of Interest as Ram- or Turbo-Rocket Fuels.

	Monopropellant Adiabatic Flame Temperature (^oF)	Monopropellant Specific Impulses	Product of Density and Monopropellant Specific Impulse $(\frac{g.sec.}{cm^3})(\frac{lb.sec.}{ft^3})$	
acetylene	5103	2??.0	145.3	9,070
methylacetylene	2646	192.7	129.3	8,074
1,5-hexadiyne	3230	188.6	151.1	9,430
1,6-heptadiyne	2600	179.4	144.4	9,017
1,7-octadiyne	2100	167.0	136.4	8,519
methylvinylacetylene	2040	162.3	110.4	6,890
methyldivinylacetylene	1740	141.9	110.8	6,919
cyclopropylacetylene	2440	177.3	137.1	8,557
cyclopropylvinyl-acetylene	2132	156.8	129.2	8,062
ethylene oxide	1728	169.0	147.2	9,190
epoxybutyne	3072	191.6	181.1	11,300
1,2-epoxyhexen-5-yne-3	2433	170.8	-	-
2-methyl-1,2-epoxyhexen-5-yne-3	1983	159.8	147.0	9,170
methylepoxybutyne	2168	170.8	152.7	9,532
dipropargyl amine	3140	194.2	175.0	10,920
dipropargyl ether	2958	187.0	172.8	10,790

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Table III

Fuel Specific Impulse Values for Selected Compounds.

Compound	Air to Fuel Ratio * $\left(\dfrac{\text{Pound of Air}}{\text{Pound of Fuel}}\right)$	Fuel Specific Impulse (S_F) (sec)	Product of Density and Fuel Specific Impulse $\left(\dfrac{\text{lb.sec}}{ft^2}\right)$	$\left(\dfrac{g.sec.}{cm^3}\right)$
acetylene	-	2331	90,350	1447
methylacetylene	13.73	2406	100,800	1615
1,5-hexadiyne	13.20	2320	116,000	1858
1,6-heptadiyne	13.43	2348	118,000	1890
1,7-octadiyne	13.57	2362	120,500	1930
methylvinylacetylene	13.51	2350	99,760	1598
methyldivinylacetylene	13.51	2330	113,600	1820
cyclopropylacetylene	13.49	2351	113,400	1817
cyclopropylvinyl- acetylene	13.41	2326	119,650	1917
ethylene oxide	7.80	1429	77,710	1245
epoxybutyne	9.08	1616	95,340	1527
1,2-epoxyhexen-5-yne-3	10.23	1817	-	
2-methyl-1,2-epoxyhexen- 5-yne-3	10.79	1906	109,500	1754
methylepoxybutyne	10.03	1795	100,100	1605
dipropargyl amine	11.42	2032	114,300	1831
dipropargyl ether	10.21	1020	105,460	1689
JP-4 (taken as dodecane, $C_{12}H_{26}$)	14.92	2327	108,950	1745

* Stoichiometric requirement of air for complete combustion of fuel employed.

S_F is based on liquid fuel at $25^{\circ}C$.

$P_{chamber} = 14.7$ psia

Expansion to Mach 1 at exit. Air intake at $25^{\circ}C$.

The products of the fuel specific impulses and the densities (density fuel impulses) are also presented.

In order that some comparison can be made between the fuel impulse values for acetylenic compounds and the standard ram jet fuel JP-4, the corresponding values for JP-4 have been calculated and are incorporated into Table III.

If one considers the fuel specific impulse values alone it appears that only the acetylenic hydrocarbons compare favorably with JP-4, and methylacetylene would appear to be the best of the compounds listed. The presence of nitrogen or oxygen in the molecule results in a decrease in the fuel specific impulse. However, if one takes the densities of the fuels into account, as was done in the previous section of this paper, some very significant facts become obvious.

From a comparison of the products of the fuel specific impulse values and the densities, it can be seen that the value for methylacetylene is significantly lower than that for JP-4, and it must be remembered as stated previously that the true value for methylacetylene is somewhat lower than that listed in Table III.

It is also evident that many of the acetylenic fuels compare very favorably with JP-4, and appear to be of greater value than either methylacetylene or ethylene oxide.

As was noted in the discussion of the compounds as monopropellants, here it also appears that the relatively high densities of those compounds that contain either nitrogen or oxygen tend to balance their apparently lower fuel specific impulse values.

Acetylenic Compounds as Additives to Methylacetylene

It has been mentioned that although methylacetylene has a high monopropellant specific impulse and a high fuel specific impulse, it suffers from the disadvantages of having a high vapor pressure and a low density. One way of overcoming these difficulties would involve blending methylacetylene with other high energy compounds that have lower vapor pressures.

The vapor pressures of a number of blends were calculated according to Raoult's Law, and the monopropellant specific impulses were calculated for those blends which have vapor pressures of 60 psia at $100°F$. The data for some of the propyne blends are given in Table IV.

Table IV

Monopropellant Specific Impulse Values for
Some Binary Mixtures Containing Propyne.

Additive	Minimum weight percent of additive required to reduce vapor pressure to 60 psia at 100°F.	Specific Impulse at concentration corresponding to 60 psia *	Maximum amount of additive which can be present and still have $I_{sp} \geq 170$
1,3-Pentadiyne	61.0	187.0	100.0
1,3-Hexadiyne	65.3	184.3	100.0
1,5-Hexadiyne	65.6	190.0	100.0
Methylvinylacetylene	68.4	171.9	74.6
1,6-Heptadiyne	68.9	183.5	100.0
Methyldivinylacetylene	69.0	157.7	44.7
Divinyldiacetylene	70.8	176.4	98.7
1,7-Octadiyne	71.7	174.3	88.3

* This is also the maximum specific impulse which the propyne-binary system can attain and still satisfy the vapor pressure requirement.

The following factors are also listed in Table IV:

a) The minimum amount of "additive" required to reduce the vapor pressure to 60 psia, and the specific impulse corresponding to this minimal value, and

b) The maximum amount of additive which can be added to propyne and still satisfy the specific impulse requirement of 170 seconds. In instances where the specific impulse of the additive is greater than 170, the figure tabulated is 100% additive.

The only binary system which cannot simultaneously satisfy the minimum requirements for specific impulse and vapor pressure is the system methylacetylene-methyldivinylacetylene. All other mixtures are satisfactory in the composition ranges noted in Table IV, e.g. 1,6-heptadiyne is satisfactory when present from 68.9 to 100 percent by weight.

General Properties of Acetylenic Compounds.

In addition to the general physical and thermodynamic properties of the acetylenic compounds, certain other properties which are associated with handling characteristics are of considerable im-

portance; these include storage and shock stability, toxicity, and compatibility with various materials of construction.

Storage Stability

Deterioration during storage is mainly caused by polymerization and peroxidation. In general, those acetylenic compounds that are not conjugated and contain no double bonds are the most stable. A series of tests have been run to determine the relative stabilities of many of the acetylenic compounds. Samples were heated at 71°C. for five days, and were then analyzed for polymer content; the results of these tests are listed in Table V.

Similar tests were conducted using mixtures of methyl-acetylene with:

> 1,6-heptadiyne (69.0%)
> 1,7-octadiyne (72.0%)
> methyldivinylacetylene (68.9%)
> divinyldiacetylene (71.0%)
> methylvinylacetylene (68.9%).

The solutions of 1,6-heptadiyne and 1,7-octadiyne in methyl-acetylene are stable in the presence of hydroquinone. The others show greater tendencies to polymerize, and in the case of divinyl-diacetylene this seems to be sufficient to exclude its use in fuel blends. On the basis of past experience, it appears that 1,3-pentadiyne and 1,3-hexadiyne would also polymerize too rapidly to be practical for use.

Shock Sensitivity

In the N.Y.U. Laboratories a mechanical impact test apparatus has been used to measure the shock sensitivity of many compounds. This apparatus which has been previously described (6), consists of a steel ball dropping on a piston which adiabatically compresses the test fuel in a small cylinder. This test indicates whether a compound will detonate under the prescribed conditions but does not rate a non-detonating compound. In order to do this, a procedure was developed in which the tester is used to determine the amount of dilution with a shock sensitive material technical grade 2,2-bis (tertiary butyl peroxy butane) required to cause detonation of the test material. A value of 40, for example, would mean that addition of 40% of the acetylenic compound quenched the detonation of the peroxy butane. The results of many of these tests are listed in Table VI. None of the compounds listed there could be detonated in the undiluted state by this test.

A second method of determining shock sensitivity was used in a series of tests which were run at Picatinny Arsenal by New York University. In this test, the compound is subjected to the
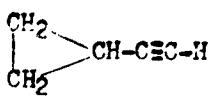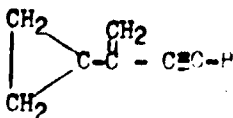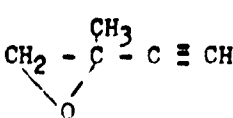
Table V

Storage Stabilities of Selected Acetylenic Compounds
Conditions: Storage at 71°C. for Five Days.

Compound	Structure	Remarks
1,6-heptadiyne	$H-C{\equiv}C-CH_2-CH_2-CH_2-C{\equiv}CH$	Very stable; only a trace of polymer isolated.
1,7-octadiyne	$H-C{\equiv}C-CH_2-CH_2-CH_2-CH_2-C{\equiv}C-H$	Very stable; only a trace of polymer isolated.
methyldivinyl-acetylene	$CH_2{=}\overset{CH_3}{C} - C{\equiv}C-\overset{\text{ }}{C} = CH_2$	Pure compound undergoes extensive polymerization, but the addition of 0.3% Quinhydrone reduces the amount of polymer formed to about 1% by weight.
methylvinyl-acetylene	$CH_2{=}\overset{CH_3}{C} - C{\equiv}CH$	Less stable than methyldivinyl-acetylene.
cyclopropyl-acetylene	$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}{>}CH-C{\equiv}C-H$	Forms 1% polymer by weight.
cyclopropyl-vinylacetylene	$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}{>}C-\overset{CH_2}{\underset{}{C}} - C{\equiv}C-H$	Quite unstable; 50% polymer formed. Quinone does not inhibit polymerization.
methylepoxybutyne	$CH_2 - \overset{CH_3}{\underset{\diagdown O \diagup}{C}} - C \equiv CH$	Very stable. Trace of polymer formed.
dipropargyl ether	$H-C{\equiv}C-CH_2-O-CH_2-C{\equiv}C-H$	Very stable. Trace of polymer formed.

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extreme shock of a detonating blasting cap. This is accomplished
by placing the test material in a test tube which in turn is placed
inside a snugly fitting lead pipe; a number 6 blasting cap is
lowered into the test tube, and the entire apparatus is detonated
behind appropriate barriers. The extent of detonation can be es-
timated from the degree of fragmentation of the lead pipe.

The results obtained using these two methods of measuring
shock sensitivity were found to be in good agreement.

Table VI

Mechanical Impact Sensitivity Values

Compound	Mechanical Impact Sensitivity Rating
1,6-heptadiyne	50
1,7-octadiyne	40
methylvinylacetylene	40
methyldivinylacetylene	50
cyclopropylacetylene	40
cyclopropylvinylacetylene	70
1,2-epoxybutyne	40
2-methyl-1,2-epoxybutyne	50
dipropargylamine	70-80
dipropargyl ether	70

Mechanical impact sensitivity tests also were run on mix-
tures of methylacetylene with: 1,6-heptadiyne (69.0%; 1,7-octadiyne
(72.0%); methyldivinylacetylene (68.9%); divinyldiacetylene (71.0%)·
and methylvinylacetylene (68.9%). No detonations were observed for
any of the mixtures.

Toxicity

Only a limited amount of information is available concerning
the toxicological properties of acetylenic hydrocarbons. Some re-
search has been conducted on methylvinylacetylene, a compound which
may be considered as typical of its class. The toxicity of the com-
pound was determined by the intragastric and respiratory route, and
the local irritant properties were determined by placing some of the
compound into the eye of a rabbit.

It was found that the compound caused artificial sleep
(hypnosis or narcosis) in mice. The testing also indicated that the
material possesses a very slight irritative activity, and this agrees
with previously reported studies in which butadiene, isoprene and
other related compounds were said to cause irritation of mucous mem-
branes of the eye and respiratory tract.

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Using the system of classification of Hodge and Sterner
(1949) the ALD value (Approximate Lethal Dose) following oral admin-
istration of methylvinylacetylene indicates that the compound has a
rating of "slightly toxic". It appears that any industrial hazard
involved in the handling of the compound would lie in its action as
a hypnotic and narcotic agent. As indicated by results on related
compounds, prolonged breathing of high concentrations could result
in irritation of the respiratory passages.

Corrosion

In general, it appears that most of the acetylenic com-
pounds described herein are not corrosive to common metals. Other
compounds such as propargyl chloride and propargyl bromide which
contain reactive halogen atoms might be corrosive due to the liber-
ation of halogen acids on hydrolysis, but the hydrocarbons, ethers,
alcohols and epoxides appear to be relatively inert. Air Reduction
Co. has come to similar conclusions regarding certain acetylenic
hydrocarbons.

Logistics

The logistics of any new fuel are of the greatest import-
ance in determining its final usage. The higher acetylenic hydro-
carbons may be produced by a number of techniques, several of which
have been shown to be of potential commercial applicability (7).
A most reasonable method of producing vinyl acetylenic compounds
involves the condensation of a terminal acetylenic hydrocarbon with
a ketone such as acetone in the presence of a slurry of solid potas-
sium hydroxide as catalyst. The resulting acetylenic alcohol may
then be dehydrated to the hydrocarbon. A typical reaction is illus-
trated by the following equation:

$$R-C\equiv CH + CH_3-\underset{O}{\overset{}{C}}-CH_3 \quad \frac{(1)\ KOH\ Slurry}{(2)\ Hydrolysis} \quad R-C\equiv C-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

$$R-C\equiv C-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-H_2O} R-C\equiv C-\overset{CH_3}{C}=CH_2$$
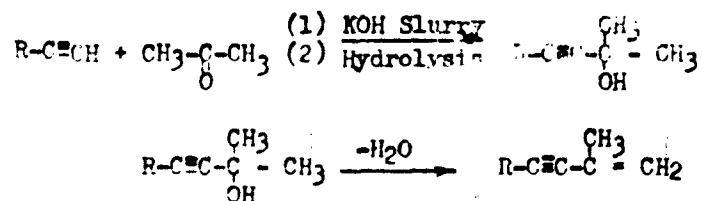
Acetylenic compounds such as 1,6-heptadiyne can be pro-
duced by the condensation of the sodium salts of acetylenic compounds
with aliphatic halides; e.g.

$$2R-C\equiv C-Na + X-R'-X \rightarrow R-C\equiv C-R'-C\equiv C-R + 2NaX$$

Acetylenic ethers can be formed using a Williamson-type
synthesis which involves the reaction of a halide with the sodium
salt of the alcohol. Propargyl ether can be prepared from propargyl
alcohol, propargyl bromide and potassium hydroxide.

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$$H-C\equiv C-CH_2-Br + H-C\equiv C-CH_2OH + KOH \rightarrow H-C\equiv C-CH_2-O-CH_2-C\equiv CH + KBr$$

$$+ HOH$$
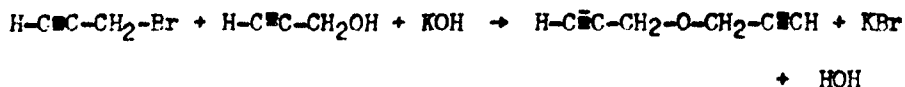
The epoxyacetylenic compounds can be produced by the oxidation of acetylenic hydrocarbons that also contain double bonds. The double bond can be preferentially oxidized to an epoxide group.
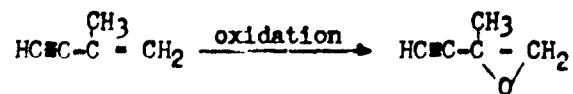
Conclusions

It is apparent that in the ram rocket and turbo-rocket it is desirable to use fuels which have both good specific impulses as monopropellants and which give rise to exhaust products which have high heats of combustion with air. In these respects methylacetylene offers considerable merit as a fuel, but it has the disadvantage of high vapor pressure and low density. The disadvantage of high vapor pressure can be minimized by using relatively non-volatile, high energy additives. Several acetylenic hydrocarbons show promise in this respect.

In certain missile applications where space considerations are of paramount importance, it is desirable to have a maximum amount of thrust available from a minimum volume of fuel. For such applications certain acetylenic compounds that contain either oxygen or nitrogen, e.g. propargyl ether, dipropargyl amine, appear to have distinct advantages.

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IMPROVEMENTS IN THE OPERATING CHARACTERISTICS
OF n-PROPYL NITRATE

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ABSTRACT

This paper summarizes chemical aspects of the work done at the Aerojet-General Corporation in the past year in the development of a gas generator-turbine combination employing n-propyl nitrate. The methods employed to reduce the chamber temperature and carbon formation are described. The results of this work lead to the use of the additive ferrocene which successfully eliminated carbon deposition. Attempts to reduce the chamber temperature were only partially successful and an external coolant was used to reduce the turbine gas temperature to a more acceptable level. Attempts to propagate a detonation through tubes containing n-propyl nitrate and tests to determine the minimum amount of an inert gas to prevent the inflammation of n-propyl nitrate in air are also described.

INTRODUCTION

A monopropellant used for power generation possesses an advantage over bipropellants because of the saving of weight. Monopropellants that have been primarily considered are nitromethane, n-propyl nitrate, hydrazine, unsym-dimethylhydrazine, ethylene oxide, nitroethane, hydrogen peroxide, and substituted acetylenes. During the past several years Aerojet-General has been actively engaged in the development of hardware for power production utilizing n-propyl nitrate and ethylene oxide. Each monopropellant has its own problems associated with it. For example, typical disadvantages of some monopropellants are as follows:

Hydrazine -- difficult to start without a catalyst bed.

Ethylene oxide -- polymerization, high vapor pressure, carbon formation.

n-propyl nitrate -- high flame temperature, carbon formation.

This discussion is limited to the chemical problems associated with n-propyl nitrate, which was chosen for use in a gas generator. The combustion products expand through a de Laval nozzle and drive a high-speed turbine coupled to an electric generator. The varying power required by the system is controlled by changing the fuel flow. This requirement means that satisfactory operation of the gas generator must be obtained over a chamber pressure range of 300 to 1200 psig for an extended period. In addition, the system must operate at both low and high monopropellant temperatures.

The two most important problems involved in the use of n-propyl nitrate are the high chamber temperature and its tendency to deposit carbon in the chamber. In the gas generator used for this study the carbon fouls the injector and nozzle so that satisfactory operation is possible for only a short time. The high chamber temperature, which is approximately 2350° F, necessitates the use of Haynes-25 alloy for chamber construction, but an even more important factor is the high temperature in the turbine. The problem is therefore to devise a method of reducing or eliminating the carbon deposition and also to reduce the temperature of the gas entering the turbine. These two tasks, which are not distinct problems, are discussed in the paragraphs that follow. Finally, some tests concerning the safe handling of n-propyl nitrate are described, namely attempts to initiate a detonation wave in tubes filled with the liquid and the amount of an inerting atmosphere required to prevent ignition of n-propyl nitrate-air mixtures by a hot surface.

TECHNICAL DISCUSSION

The chamber temperature which will be attained when a mono-propellant decomposes under adiabatic conditions can be calculated, provided that there is ample time for the propellant gases to come to equilibrium. Such calculations have been made for n-propyl nitrate assuming that the products are only CO, CO_2, H_2, H_2O, N_2, H, CH_4, and solid carbon. A typical calculation (Reference 4) shows that at 800 psia and 1300° K (1880° F) the gas consists mostly of carbon monoxide and hydrogen and has the following composition:

	Vol. Percent
CO	36.4
CO_2	3.4
H_2	38.7
H_2O	6.7
N_2	8.3
CH_4	6.5
TOTAL	100.0

Solid carbon = 0.97 grams/ 100 grams of gas

A heat balance, assuming these products, yields an adiabatic chamber temperature of $1350°$ K ($1970°$ F), whereas the measured chamber temperature at Aerojet-General and elsewhere (Reference 5) is in the range 2300 to $2400°$ F.

Flame temperatures higher than the theoretical value can be calculated if one assumes methane to be present in the gas mixture in amounts greater than the theoretical amount. In fact, a higher flame temperature will result if other hydrocarbons or ammonia are present. As has been pointed out by others (Reference 5), the temperatures attained are relatively low so that kinetic equilibrium of the various species is not obtained.

As an example of the complexity of the decomposition process some of the reactions that have been studied kinetically are shown in Figure 1, starting with n-propyl nitrate vapor. At the relatively low temperature of $180°$ C the decomposition products from n-propyl nitrate are n-propyl nitrite and nitroethane. The kinetics of the decomposition of n-propyl nitrite (Reference 2) and of propylene (Reference 3) have also been studied; the final products from propylene being hydrogen, methane, ethylene, acetaldehyde, acetylene, benzene and toluene. The illustrated steps in Figure 1 are obviously not the only ones possible. For example, nitrogen dioxide and nitroethane can oxidize any of the hydrocarbons present and the aldehydes would further decompose to simpler species.

The carbon formation can occur through any one of a series of steps, the simplest being the disproportionation of carbon monoxide at a dull red heat:

$$2 \text{ CO} \rightleftharpoons \text{C} + \text{CO}_2$$
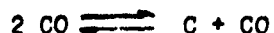
or carbon may be formed by the cracking of acetylene, ethylene or cyclic hydrocarbons. In fact, the carbon may come from a multitude of different reactions (Reference 6). The picture is further complicated by the fact that many of these reactions are influenced by catalysts and yield different products depending on the influence of the container walls. In summary, the two problems of reducing the amount of coking and simultaneously reducing the adiabatic chamber temperature are intimately related and the solution of one will not necessarily solve the other. Furthermore, the complexity of the thermal decomposition process makes it extremely difficult to predict the effect of any specific scheme to solve the problem.

In the paragraphs that follow, the experimental set-up is described together with the program plan and the results obtained.

EXPERIMENTAL METHOD

The equipment used was a cylindrical gas generator constructed of Haynes 25 alloy with a pin-jet injector and with an 800-inch L*.

No major changes in the chamber configuration were made during this program. The n-propyl nitrate flow rate was approximately 2 lbs/min. An air start with glow plug ignition was used. The gas temperature and the outside wall temperature were taken during the run. The chamber pressure during the tests ranged from 800 to 1200 psig. The weight and character of the carbon were also noted after the completion of the run.

PROGRAM PLAN

Reduction of Chamber Temperature

Two substances which should reduce the chamber temperature by absorbing heat are dioctyl sebacate /di-2-ethyl hexyl sebacate/ or polyethylene glycol, which were tried at the U. S. Naval Underwater Ordnance Station. (Reference 5, p. 242) The dioctyl sebacate was reported to be capable of lowering the temperature to 1400° F, but polyethylene glycol was a better performer. In addition to these suggested compounds others were tried that should decompose to give carbon dioxide, such as diethyl oxalate and diethyl carbonate. Croll (Reference 7) has reported that steam reduces the amount of coke formation during the cracking of hydrocarbons in an iron tube. Therefore, water, a low-freezing emulsion of ethylene glycol plus water in n-propyl nitrate, and various alcohols were also suggested for trial.

Another suggestion for lowering the flame temperature comes from the reported inhibition by halogen compounds of the oxidation of carbon monoxide during the combustion of the carbon in air. Concentrations varying from 0.1 to 2% of compounds such as $POCl_3$, PCl_3, Cl_2, CCl_4, $CHCl_3$, $SnCl_4$, CH_2Cl_2, HCl and I_2 were reported to be very effective (Reference 8). If carbon monoxide oxidation could be inhibited in the gas generator, the chamber temperature should be decreased. Therefore, some of these halogen compounds were tried as additives.

The results of some of the many tests that were made are shown in Table 1. Nearly all of the trials resulted in carbon formation so that accurate thermocouple readings were not always obtained; nevertheless no really satisfactory reduction in chamber temperature was obtained.

Reduction of Carbon Formation

At the same time that experiments on temperature reduction were performed, attempts were made to find additives to reduce coking. The program plan for the reduction of the coking problem was first to search the available literature for the solution of analogous problems. For example, there is an enormous amount of literature on the problem of coking during the thermal cracking of hydrocarbons. The effect of steam in preventing coking has

already been mentioned. Substances such as carbon disulfide and dimethyl sulfoxide, which reduced carbon formation in an ethylene oxide gas generator (Reference 5, p. 177), were also tried. Combustion catalysts, such as the acetylacetonates of iron, copper and manganese were used to determine whether this would result in a reduction of the carbon deposits. Additives have been found useful in reducing carbon deposits in turbojet engines. For example, Jonash and Cook have tested additives such as commercial fuel oil additives, lead additives, cadmium naphthenate, and ferrocene (dicyclopentadienyl iron II) to prevent coking of the burners /Reference 9/. The authors state that there is probably an optimum concentration for each of these additives and that ferrocene was the best additive found when used at a concentration of 0.05 weight per cent.

A partial list of the additives tried at Aerojet-General is shown in Table 2. The results of these tests can be summarized as follows: None of the compounds tried resulted in a satisfactory reduction in carbon deposition with the exception of carbon tetrachloride and ferrocene. In the case of carbon tetrachloride, runs of a duration less than six minutes gave no carbon, but considerable carbon was formed in longer runs. It appears that the rate of carbon formation in this instance accelerates with time. The results obtained with ferrocene were completely satisfactory for the required duration, the only carbon formed being a thin dust on the chamber walls. However, ferrocene is not stable in n-propyl nitrate so that it is also necessary to add a stabilizer to obtain a solution that can be stored for long periods at elevated temperatures.

Because the hydrocarbon dicyclopentadiene used as an additive did not prevent carbon deposition, the cause must be attributed in some way to the iron. The ferrocene does not alter the chamber temperature which would be expected f the ferrocene altered the gas composition markedly, nor is it known whether the ferrocene prevents the formation of carbon or merely prevents it from forming agglomerates that can stick to a metal surface. In the hope that other effective additives containing iron could be found, ferric acetonylacetate was re-investigated over a wider concentration range than previously used. The best concentration found was between 0.05 and 0.10%, but the results were inferior to those obtained with ferrocene.

After the utility of ferrocene was shown, the search for a suitable temperature depressant continued. Concentrations of isopropyl alcohol above 15 wt % resulted in ignition difficulties and use of 10 wt % of Ucon oil resulted in abnormal operation at low chamber pressures. Because the use of a temperature depressant dissolved in the n-propyl nitrate did not result in an operating temperature below 2000° F without creating problems of ignition and stable operation, this approach was abandoned. Cooling of the turbine gases was achieved by injection of a separate stream of coolant gas into the turbine.

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In summary, a method of successfully preventing carbon deposition was achieved by the use of ferrocene plus a stabilizer for this particular gas generator configuration, but no means of reduction of the chamber temperature by using diluents was satisfactory. In the future it would be desirable to obtain chamber gas analyses over a range of operating pressures with and without ferrocene and at various values of the characteristic length, L^*, in order to obtain a better insight into the mechanism of carbon deposition.

PROPELLANT SAFETY

Several types of tests have been made in the last year on the safe handling of n-propyl nitrate. These are (1) adiabatic compression, (2) attempts to propagate a detonation wave through liquid n-propyl nitrate and (3) measurements of the amount of inert gas such as nitrogen, carbon dioxide, or Freon 13B1 required to prevent the ignition of n-propyl nitrate-air mixtures on a hot surface. The detonation propagation tests and the ignition tests are described briefly below.

In order to determine the ease of propagation of a detonation in liquid n-propyl nitrate at 300° F, the ability of a detonation wave to pass two right angle bends in stainless steel tubing was measured. The apparatus in which the tests were run consists of an annular reservoir filled with n-propyl nitrate. In the center of this outer reservoir is a separate container which can be filled with a liquid explosive. The reservoir containing the n-propyl nitrate is connected to a length of 1/4-in. stainless steel tubing, in which two right angle bends were made about 4-in. apart. The outer reservoir and tubing were filled with n-propyl nitrate, the apparatus was then sealed and heated to 300° F. A test tube containing a quantity of Aerex (a proprietary Aerojet liquid explosive) and an initiator were lowered into the upper, inner reservoir and detonated. In the tests conducted in this manner no propagation of the detonation wave was observed in the n-propyl nitrate because the 1/4-in. tubing was recovered intact in each case, and liquid was found remaining in the 1/4-in. tubing. As a means of comparison, the 1/4-in. tubing and the outer reservoir were filled with Aerex explosive, which, through previous experience, is known to propagate a detonation wave, and initiated in a similar manner. Shreds of the 1/4-in. stainless steel tubing were all that could be found after the test. Therefore, it is concluded that liquid n-propyl nitrate at 300° F does not propagate a detonation in a 1/4-in. tube. These tests were extended to tubes of larger diameter, namely 1/2-in. and 1-1/4-in. and in these tests no detonation propagation was observed. It is concluded, that in the event of a malfunction in the gas generator, a detonation wave will not propagate back to the storage vessel, even through tubes larger than customarily used.

CONFIDENTIAL

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Another possible hazard that is being investigated is the behavior of n-propyl nitrate sprayed against a hot metal surface in an atmosphere consisting of air mixed with either nitrogen, carbon dioxide, or Freon 13B1 (bromotrifluoromethane). The original apparatus consisted of a 230 ml glass tube containing a hot stainless steel target against which liquid n-propyl nitrate was injected with a hypodermic needle. More recently, a larger apparatus of 12.8 liters volume was constructed with a window in one end. The parameters studied were the temperature of the atmosphere surrounding the plate, the stainless steel plate temperature, the composition of the gas mixture, the amount of n-propyl nitrate injected against the plate, and the incidence of flame. The total pressure before injection of the liquid n-propyl nitrate was 14.7 psia. The results of some of these tests are shown in Table 3. These tests indicate that for a plate temperature of 800 to 940° F and a gas temperature of 400 to 500° F the following concentration of inert gas must be used to prevent inflammation:

Nitrogen — 75 to 87 vol %

Carbon dioxide — 50 to 63 vol %

Freon 13B1 — 50 to 75 vol %

However, it is known that if the gas temperature were equal to the plate temperature the amount of inerting gas would have to be raised to prevent combustion. These studies are being continued, using higher concentrations of n-propyl nitrate and higher plate temperatures.

ACKNOWLEDGMENTS

CONFIDENTIAL

Lawrence, Knight

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TABLE 1

ADDITIVES TRIED FOR TEMPERATURE REDUCTION IN A n-PROPYL NITRATE GAS GENERATOR

Additive	Wt %	Chamber Temperature °F
None	—	2350
Isopropyl alcohol	8.0	2200-2300
Ethylene oxide	20.0	1800-2100
Ethylene oxide	10.0	2100-2200
Water	5.0	2250
Dioctyl azelate	10.0	1900-2000
Freon 113	5.0	2300
Diethyl oxalate	5.0	2190
Diethyl oxalate	10.0	2140
Diethyl carbonate	10.0	2000
Dimethyl disulfide	4.5	2030
Dimethyl formamide	4.5	1760
Ethylene carbonate	5.0	1900
Carbon tetrachloride	5.0	2300
Chloroform	5.0	2250
Dimethyl sulfoxide	2.0	2130
Dioxane	5	2130
Tetraethyleneglycol dimethyl ether	5	2040
Ethyl formate	10	2130
Dioctyl sebacate (+ 0.1% carbon tetrachloride)	5	2100*
Dioctyl sebacate (+ 0.05% ferrocene)	5	2150*
Ucon Oil, 50HB260 (+ 0.05% ferrocene)	10	2000*

* No carbon formation.

TABLE 2

ADDITIVES TRIED TO REDUCE CARBON FORMATION IN A
n-PROPYL NITRATE GAS GENERATOR

Additive	Wt %	Duration, Min	Carbon Formation
Cobalt octoate	2.0	6	Large
Carbon disulfide	2.0	6	Moderate
Dimethyl sulfoxide	2.0	6	Moderate
Tetraethyl lead	2.0	2	Small
Carbon tetrachloride	0.10	6	Nil
Iodine	0.75	1-1/2	Large
Dicyclopentadiene	0.05	6	Large
Ferrocene (+ 0.1% stabilizer)	0.05	16	None
Ferrocene (+ 0.1% stabilizer)	0.01	13	None
Ferric acetylacetonate	0.005	12	Moderate
Ferric acetylacetonate	0.01	3	Moderate
Ferric acetylacetonate	0.05	11	Small
Ferric acetylacetonate	0.10	11	Small
Ferric acetylacetonate	2.0	——	Large
Manganese acetylacetonate	0.20	6	Large

Lawrence, Knight

TABLE 3

INCIDENCE OF IGNITION FOR n-PROPYL NITRATE INJECTED AGAINST A METAL PLATE IN VARIOUS ATMOSPHERES

Gas Temp. °F	Plate Temp. °F	Vol % Air	Vol % N_2	n-PN, ml	Number of Tests	
					Total	Combustion
275-325	800-940	25	75	2.0	14	3
415-450	900-910	25	75	2.0	5	5
415-450	800-900	12.5	87.5	1.0	11	0
		Vol % Air	Vol % Freon			
415-455	875-900	25	75	2.0	5	0
430-440	850-865	50	50	2.0	5	3
425-435	815-850	37.5	62.5	2.0	5	4
415-440	795-780	25	75	2.0	3	0
415-440	745-780	25	75	1.0	3	0
440-440	770-790	32	68	1.0/2.0	5	0
		Vol % Air	Vol % CO_2			
420-450	890-900	25	75	2.0	5	0
420-450	900-925	37.5	62.5	2.0	5	0
425-450	925	50	50	2.0	3	3
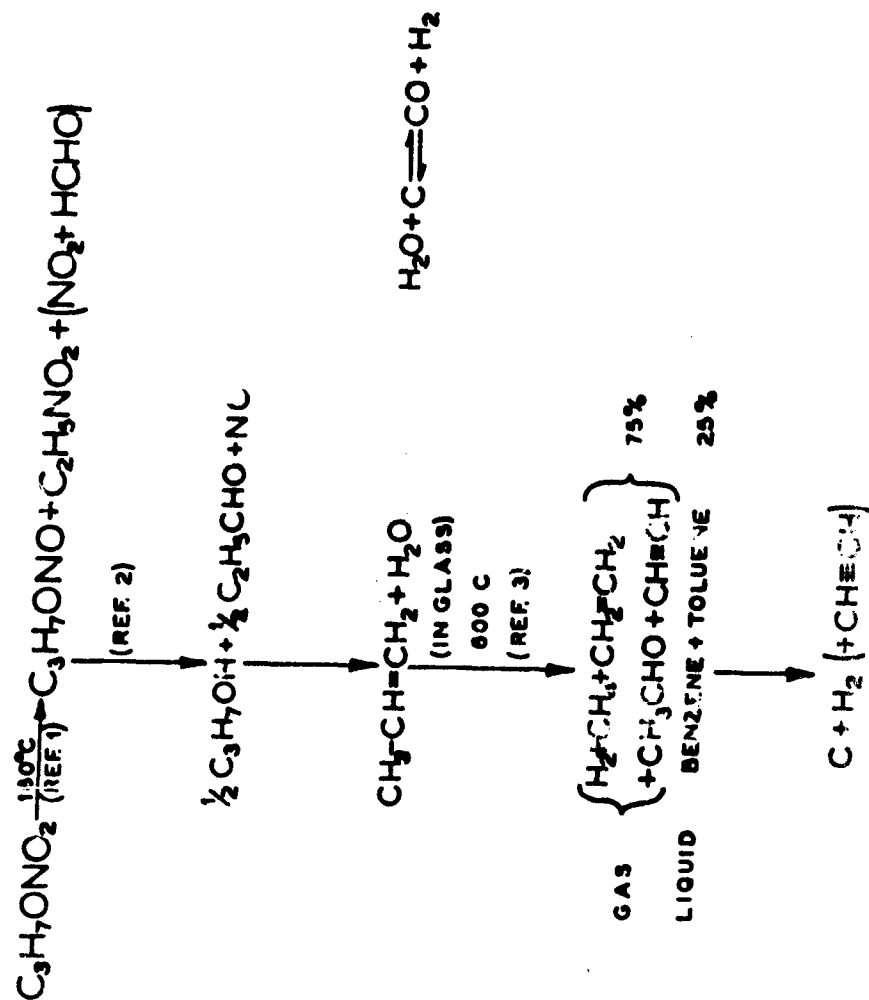
FIG. 1   SOME POSSIBLE DECOMPOSITION PRODUCTS OF N-PROPYL NITRATE AT PROGRESSIVELY HIGHER TEMPERATURES

PROPOSED TEST FACILITY
FOR 100,000 POUND THRUST ROCKETS
UTILIZING LIQUID FLUORINE

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INTRODUCTION

The military requirement for placing a large payload in space by the use of a small low-cost missile structure has placed new demands on the development of improved rockets. Investigation of how to achieve improved rocket performance has led to the consideration of high energy propellants. Although there are many propellants that are capable of being used for their high specific thrust, still there are only a few that can be used in a practical design. At this time, fluorine-type oxidants are considered capable of attaining the requirements of an operational missile. It is this assumption that has prompted the following discourse on a test facility capable of testing a fluorine rocket.

Liquid fluorine vaporizes so rapidly and has such violent chemical reactivity that complex methods are required to neutralize it in the liquid state. In its vapor state fluorine forms a gas cloud of high toxicity, and natural atmospheric diffusion is the only known method of reducing the hazards of the airborne cloud. Even after fluorine undergoes combustion, its products of combustion contain the highly poisonous gaseous hydrofluoric acid. In addition, hydrofluoric acid will attack glass, concrete, certain metals, natural rubber, leather, and many organic materials.

In spite of the above disadvantages, the use of fluorine is necessary because of the structural problems and restricted performance imposed by the use of conventional rocket oxidizers.

In order to reach targets on another continent, it is necessary for a rocket utilizing conventional propellants to burn three-quarters of a ton of propellants during each second of powered flight. This high flow rate of propellants being pumped through the combustion chamber is made possible by the turbine being able to withstand, during its 500 seconds lifetime, the thermal weakening of structures when exposed to the hot impinging gases of 1,200°F (standard steels lose their structural properties at 1,200°F), and the centrifugal stresses imposed by turbine rotational speeds of 30,000 RPM (piston-

driven propellers rotate at 2,500 RPM, axial-type turbines in turbojets rotate at 8,000 RPM, and centrifugal-type turbines rotate at 12,000 RPM). Thus it is clear that heavier payloads and longer ranges would necessitate stretching performance of missile components to beyond the state of the art or else using excessively large structures.

The use of high energy propellants will permit futuristic accomplishments to be achieved. For example, if the 1,500 pounds of payload were to be delivered to a long range target by a high energy propellant combination (T_{sp} = 275 seconds) instead of a conventional propellant combination (T_{sp} = 250 seconds), then the propellant flow rate requirement drops 57%, the diameter of a 100 feet long missile shrinks 33%, the maximum drag force reduces 84% (lower drag means lower propellant requirements, smaller structures to accommodate the lower propellant requirement, and lower skin temperature), and the over-all weight decreases 54%. For a more detailed comparison, reference Appendix A of this report.

Thus, if longer ranges and heavier payloads are to be achieved by future missiles, then the improved performance capability of new propellant combinations must be tried in spite of the many hazards involved in harnessing the higher specific thrust propellant combination.

The harnessing of fluorine as a rocket propellant has been accomplished by the National Advisory Committee of Aeronautics with their 5,000 pound thrust rocket, the Rocketdyne Division of North American Aviation, Incorporated, with their 5,000 pound thrust rocket, and the Bell Aircraft Corporation with their 30,000 pound thrust rocket. The Rocket Engine Test Laboratory has been on contract with the General Chemical Division for a fluorine generating plant and associated facilities; with the Ralph M. Parsons company, Incorporated, for a 100,000 pound thrust fluorine rocket engine test stand and back-up facilities; and with the Stanford Research Institute for a study of the concentration of rocket toxic exhaust gases at various distances from the test site.

The purpose of this paper is to explain and describe a testing facility capable of supporting a fluorine-hydrocarbon liquid propellant rocket engine of up to 100,000 pounds thrust.

PRINCIPLES GOVERNING DESIGN OF A FLUORINE FACILITY

Fluorine, in order to exist in its liquid state, must be maintained at temperatures colder than -304.6°F at 1 atmosphere. Since liquid nitrogen at -320.4°F is used as the refrigerant and thermal insulation jacket, there are introduced hydraulic and cryogenic problems such as the following:

 (1) It is characteristic of liquids that need only a small amount of heat energy to reach their boiling point to receive this energy for boiling from warm parts and viscous work. This results in cavitation in pumps, and geysering in pipelines.

 (2) Under wide temperature ranges it is difficult to design for thermal contraction of gaskets, valve seats, close tolerance parts, and long transfer lines.

Fluorine is highly corrosive as a liquid or gas. The method of

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containment is to allow fluorine to deliberately corrode the surfaces to be wetted, until a protective, passive fluoride film forms. The following materials can be used for fluorine containment: nickel, monel, copper, brass, bronze, stainless steel, aluminum, tin, and teflon.

The toxic characteristics of fluorine and hydrofluoric acid are such that 50 to 1,200 parts per million by volume will be dangerous to life for a 30 to 60 minutes exposure, while 1,800 p.p.m. will be fatal even for a short time exposure.[1]* This toxic characteristic of fluorine establishes the need for either of two design requirements:

    (1) Fluorine must not leave the system. In order to be contained within the storage or transfer system, it is necessary that fluorine remain in its liquid state, because the excess back pressures and hydraulic problems of two-phase flow problems need be avoided. Therefore, a refrigerant is used to maintain fluorine in the desired liquid phase. Since liquid nitrogen is readily available and inert, it is convenient to use as a refrigerant.

    (2) If fluorine or its by-products are to leave the system, then absorption and neutralization must be accomplished before venting to atmosphere. Therefore, large quantities of water are used to absorb the fluorine or its by-products, and then a bed of lime slurry is used to neutralize the diluted solution. The rigid requirement placed on this absorption and neutralization process can be realized when the maximum recommended tolerable concentration of fluorine for humans is considered to be 1 to 3 p.p.m./volume.[2] This concentration will result in slight symptoms after an eight hour exposure.

Fluorine is highly reactive and will even react explosively with water if the process takes place in a confined area. It is this consideration that has led to two design requirements:

    (1) The process of absorbing and neutralizing the fluorine and its by-products exhausted from a rocket firing requires an enclosed area to avoid toxic effects on humans and corrosion of materials in the test area. The absorbing and neutralizing process takes place in an enclosed scrubber containing a water spray where the highly reactive fluorine may combine explosively with water. Thus, the scrubber will be built so as to release the force of an explosion.

    (2) Even minute quantities of water must be purged from a fluorine system, for any water in the system will create a heat generating reaction and induce boil-off in the liquid fluorine. This rapid generation of boil-off produces pressure surges. Thus, purging of any

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*Superior numerals 215 to references at the end of the paper.

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water is required before fluorine is allowed to flow within the system. In addition, protection for the structure to withstand these surges must be designed into the system.

Pure water reacts explosively with fluorine. Therefore, the water of the test stand deluge system must contain additives to neutralize the fluorine into a salt that can be handled. Excess water must be supplied to overcome the heat of reaction, heat of solution, and poor mixing of the fluorine with the alkaline water. Thus by the addition of a base, large quantities of water can be used to safely deluge the fluorine. Until further laboratory tests are completed, ammonia will be chosen as the additive to the test stand water deluge.

Exhaust gases from the rocket contain toxic gaseous hydrofluoric acid. To prevent escape of the gaseous hydrofluoric acid into the atmosphere, it is necessary to absorb the gases in a solution where they can be handled for disposal. This is accomplished by directing the exhaust gases through multiple water sprays where the gaseous hydrofluoric acid is absorbed and diluted to a weak solution. The exact extend of HF absorption in the water sprays can not be determined until the facility is in operation and sampling techniques employed. Scale-up of existing commercial scrubber facilities indicate that at least 90% of the 100,000 pound thrust toxic exhaust gases can be absorbed.

OPERATION

Operation of the proposed fluorine test facility will be as follows:

Prior to the rocket firing a careful local weather study will be made to determine the atmospheric diffusion capability. Based on the weather survey findings, the time and duration of firing are established. Then, the normal checkout of the test rocket performance sensing, recording, and control devices, and test support equipment will be accomplished. All personnel are at duty stations in the control station blockhouse, which has an emergency ventilation system with a self-contained oxygen supply. Fluorine is fed to the missile tankage from the permanent storage. A 50,000 GPM water flow through the flame deflector and scrubber systems will be started. A few seconds later, the rocket will be fired.

During the rocket firing, the exhaust flames are to be channeled through an enclosed deflector which contains jet wheels and banks of nozzles spraying water. The deflector will turn the vertical rocket exhaust gas flow into a horizontal scrubber. It is estimated that approximately 10 percent of the rocket toxic exhaust gases escape into the atmosphere from the stack at the end of the scrubber. The remainder of the rocket exhaust gases will be absorbed by water spray and leave the scrubber as a dilute hydrofluoric acid solution. This solution will flow by gravity to an enclosed catch basin (Figures 4 and 5).

After the firing, the hydrofluoric acid solution in the catch basin is pumped to two water treatment tanks where the HF solution is mixed with quicklime and water. The resulting slurry is then gravity

fed to the settling pond. In the settling pond, a precipitate settles to the bottom of the pond and the clear water is pumped into the treated water reservoir where it is available for re-use.

DESCRIPTION OF COMPONENTS

The function of each component of the facility capable of handling fluorine and its by-products will be as follows:

The fluorine will come into the test area via railroad or mobile trailers in specially constructed tank cars or trailers. Since the toxic fluorine boil-off cannot be vented while in transit, the fluorine is maintained as a liquid by a liquid nitrogen refrigerant and vacuum-perlite insulation jacket which will surround the tank car, or trailer.

At the unloading point, a small quantity of liquid fluorine from the tank car or trailer is passed through a heating coil so that the liquid will flash to its gaseous state. The accumulation of fluorine gas in the space above the liquid surface of the liquid fluorine container pressurizes the container. The liquid fluorine will be forced at high flow rates through a transfer line to permanent storage vessels by this pressurization process.

The four 50,000-gallon storage vessels, like the railroad tank car, will have concentric jackets of liquid nitrogen refrigerant and vacuum-perlite insulation surrounding the liquid fluorine container. These storage vessels are to be set in an enclosed blast-protected bunker having a floor lined with lime. The bunker will be designed to provide for neutralization of possible fluorine leakage from manifolding and storage vessel joints.

Transfer of the fluorine to the test stand will be accomplished after checking for leaks and purging the transfer system with nitrogen to remove possible contaminants, and then evacuating the system. After the evacuation procedure, the fluorine will be pushed from the storage vessels into the missile tankage by pressurized helium at 140 psi. Upon completion of the fluorine transfer, the transfer system is purged by helium gas which forces any residual fluorine through a natural gas burner, and the combusted products will be vented to atmosphere. Thus, the transfer system will be composed of nitrogen pressure bottles, vacuum pumps, vacuum insulated transfer system, helium pressure bottles, and a natural gas burner.

The test stand will be capable of withstanding thrust loadings of up to 100,000 pounds. The fluorine test stand will resemble the standard type test stand except for the following four items:

    (1) There will be a blast shield between the rocket engine and the propellant tanks. In the event of an explosion, the blast shield shall stop shrapnel and absorb blast effects that would be capable of rupturing the propellant tankage.

    (2) The high probability of frequent explosions occurring in a research and development program justifies the use of a permanent propellant dump system. In the event of an explosion, the propellants in the test rocket tankage will be immediately channeled away from the danger

area by means of a transfer line to the propellant dump temporary storage. The temporary storage capability will be designed to provide for holding all the emptied contents of the test rocket tankage. From the temporary storage, constructed on a bed of crushed limestone, the propellants will be transferred to the test stand permanent storage. This dump procedure will eliminate the spread of an uncontrolled reaction on the test stand.

(3) The water deluge for the test stand will have 200,000-gallon capacity at a flow rate of 12,500 GPM (Figure 4). This water deluge system must be designed with recognition that water and fluorine react violently. However, it has been suggested that treated water will reduce the extent of the fluorine-water reaction. Additives under consideration are calcium carbonate, calcium hydroxide, and ammonia.

(4) Back-up of the toxic rocket engine exhaust gases from the flame deflector enclosure will be reduced by a "back-up shield" placed at the top of the flame deflector enclosure. Air, entrained by the high velocity rocket exhaust, also will help reduce the escape of the exhaust gases. However, too much air entrainment is not desirable since it creates higher mass flow through the scrubber. This high mass flow is not desirable because it does not allow sufficient time for the water spray to absorb the HF. Sufficient time for the water spray absorption of HF is obtained by excessively large scrubber cross-sectional areas that are required to cause a low velocity flow under a high mass flow condition.

The fluorine boil-off in the missile tankage will not be released to the atmosphere. Instead, it will be passed through a refrigerating coil, condensed, and returned to the missile.

The high temperature exhaust gas of the rocket will be core cooled to 200°F by a jet water wheel. The jet water wheel will be located at the center line of the rocket motor, above the flame deflector, and attached to the test stand. Over 14,000 GPM of water will spray radially inward to the core of the flame through eight water nozzles. If the water nozzles were not immersed in the flame, then the high flow rate rocket exhaust gases would carry the injected water downstream to the point of impingement before the coolant water could reach the core of the flame. Thus, the nozzles will be placed in the middle third of the flame to assure uniform cooling. The nozzles will be arranged with four nozzles for each of two levels. The nozzles are aerodynamically shaped and will be arranged with a minimum number of nozzles per level to prevent back-up of the toxic rocket exhaust gases.

The flame deflector will be of the water-film-cooled plate type. Since the deflected flames will be toxic and must not escape, it will be necessary to shroud the deflector plate so that it will take on the appearance of a flame bucket. The normal back-up of gases at the entrance to a flame bucket will be suppressed by a gas back-up shield

on the flame bucket entrance and by a bank of nozzles which sprays high velocity streams of water at 2,000 GPM, entraining particles and forcing them through the bucket in the correct direction.

The bottom of the flame bucket will be shaped so as to deflect the vertical exhaust gases into the horizontal scrubber system. This turn section also will expand the gas flow during deflection to achieve a more uniform exhaust gas flow across the scrubber cross-section.

The exhaust gases will then be channeled through a scrubber where sufficient water is added to make a 1 to 5% hydrofluoric acid solution. The mixing of approximately 90,000 GPM of water with the exhaust gas will be assured by the diameter and length of the scrubber duct (Figure 4).

The vertical discharge stack of the scrubber will trap the mist of water droplets containing dissolved HF, while the unabsorbed HF escapes into the atmosphere. The mist can be trapped by three possible design features of the stack:

      (1)   Changing the direction of the mist flow causes centrifugal forces to knock the mist against the baffled side walls of the vertical stack. The baffled side walls will retain some of the mist long enough for it to form larger droplets and fall to the bottom of the stack.

      (2)   The large cross-sectional area of the stack will slow the mist velocity down so that the mist will reside long enough to settle to the floor. A baffle arrangement further along the stack will help increase the residence time to assure settling of the mist.

      (3)   Droplets over 5 microns in diameter which are still entrained in the gas stream after the settling process will be trapped by passage through a woven monel wire mesh. Provisions will be made for washdown of the mesh after exposure to the corrosive mist.

All three of the above stack design features will be desirable. However, the pressure drops associated with the use of all three devices may cause an excessive pressure drop and back-up of the toxic gases in the scrubber system.

The dilute hydrofluoric acid will flow by gravity from the scrubber, via an open lined trench, to an enclosed catch basin. The lid enclosure of the catch basin will prevent evaporation of the toxic HF. The gunnited catch basin will have a capacity of 1,000,000 gallons (Figure 2).

The large quantities of hydrofluoric acid in the catch basin will require extensive lime storage and transfer facilities to accomplish adequate neutralization. Railroad spurs for delivery of quicklime, conveyer belts, feeding mechanisms, 125-ton capacity storage silo, and bucket elevators will be used to deliver the quicklime from the railroad delivery point to the water treating tanks (Figures 2 and 4).

The dilute hydrofluoric acid in the catch basin will then be pumped at 1,000 GPM to the two 15,000 gallon water treatment tanks. These tanks will be made of steel or redwood and contain a rotary blade mixer. Water and quicklime will then be added to the hydro-

fluoric acid solution in the water treatment tanks. Constant agitation of the mixture aids the neutralizing reaction and the resultant slurry will be gravity fed to the settling pond (Figures 2 and 4).

In the 180,000 gallons settling pond the slurry from the water treatment tanks will be allowed to form clear water by allowing the settling of a sludge of calcium fluoride. The sludge will fill the pond to capacity each year and must be/removed.

The clear water from the settling pond will be pumped at 1,000 GPM to the 2,000,000 gallon treated water reservoir. This water will be re-used for the flame coolant system, scrubber system, and scrubber water treatment system (Figure 4).

In summary, the equipment peculiar to the fluorine facility will be the following: The oxidizer permanent and temporary-dump storage and transfer system; treated water test stand deluge system; scrubber and stack; quicklime storage and transfer system; dilute hydrofluoric acid catch basin; dilute hydrofluoric acid neutralizing tanks; products of the neutralized hydrofluoric acid settling pond; treated water reservoir for flame coolant, scrubber, and neutralizing tanks; and atmospheric diffusion-capability indicators (Figures 2, 3, 4 and 5). This equipment boosts the cost of the $9,000,000 conventional oxidizer two test stand facility to $12,000,000 for the fluorine oxidizer two test stand facility (Appendix B).

CONCLUSIONS

In order for rockets to attain heavier payloads and longer ranges with small low-cost structures, it is necessary to use high energy propellants.

Of the high energy propellants, fluorine is considered capable of the earliest attainment of practicability for use in operational rockets.

In spite of the many hazards associated with fluorine, a safe fluorine test facility is within the present state of the art.

The performance limits of the fluorine facility is not predictable because of the meager data available on chemical reactions and mechanical mixing in high fluid flow systems containing fluorine and its by-products. Thus, it is necessary that the initial test firings be programmed for starting with small rockets and building up the thrust level to where atmospheric diffusion can still handle the effluent toxic gases.

Expansion of the fluorine facility to support higher than 100,000 pounds thrust fluorine rocket engines will require sampling of the fluid properties throughout the 100,000 pounds thrust system during its operation. This sampling will furnish data for determining the feasibility of the expansion of the facility.

The design of this fluorine facility is considered conservative, based on the available data.

Weather surveys need be carefully accomplished because atmospheric diffusion of toxic gases determine the selection of the test site, time of firing, and duration of firing.[5] (Appendix C and Figure 6)

The estimated cost of the proposed fluorine 2 test stand complex, during 1960, will be approximately $12,000,000, as compared to

$9,000,000 for a similar test complex utilizing conventional type oxidizers.

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APPENDIX A

NOTATION:

Symbol		Definition
A	$\left(FT^2\right)$	Cross-section area of missile
C_D		Coefficient of drag
f		"Is a function of"
g	$\left(\dfrac{FT}{SEC^2}\right)$	Gravitational constant
m	(SLUGS)	Instantaneous mass of missile
T	(POUNDS)	Thrust
T_{SP}	(SFC)	Specific thrust
t	(SEC)	Time
y	(FT)	Vertical displacement above surface of earth
ρ	$\left(\dfrac{SLUGS}{FT^3}\right)$	Density of air

Superscripts:

    •   First derivative with respect to time

    ••   Second derivative with respect to time

Subscripts:

    o   Condition existing at surface of earth

    p   Propellants

DERIVATION:

    Assuming that the effects of drag, decreasing gravitational force with altitude, variation from constant propellant flow rate, and the term $\dot{m}_p \dot{y}$ are negligible; then the vertical ascension of a rocket can be approximately represented by:

$$\ddot{y} = \frac{T - \left(m_o - \dot{m}_p t\right) g_o}{\left(m_o - \dot{m}_p t\right)} \qquad (1)$$

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$$\dot{y} = \frac{T}{\dot{m}_p} \ln\left(1 - \frac{\dot{m}_p}{m_o} t\right) - g_o t \tag{2}$$

$$y = \frac{T}{\dot{m}_p}\left\{\left(\frac{m_o}{\dot{m}_p} - t\right)\ln\left(1 - \frac{\dot{m}_p}{m_o} t\right) + t\right\} - \frac{1}{2} g_o t^2 \tag{3}$$

In the case of an actual rocket, which encounters both the effects of drag and changing gravitational pull with increasing altitude, the trajectory defined by Equations (1), (2) and (3) can still be maintained by controlling the rate of propellant burning according to Equation (4).

$$\dot{m}_p = \frac{m_o \ddot{y} + m_o g + \frac{1}{2} C_D \rho A \dot{y}^2}{T_{SP}g + tg + t\ddot{y} + \dot{y}} \tag{4}$$

where

$$m_o = f\left(m_{payload}, m_{structure}, m_{propellant}\right)$$

$$\ddot{y} = f \text{ (See Equation 1)}$$

$$g = f(y) = \left(\frac{y}{y + 21 \times 10^6}\right)^2$$

$$C_D = f(A, y, \dot{y})$$

$$\rho = f(y)$$

$$A = f(m_o)$$

$$\dot{y} = f \text{ (See Equation 2)}$$

$$T_{SP} = f \text{ (Propellant combination)}$$

As a result of the above equations, it was possible to obtain the graphical comparison shown on Figure 1 for the assumed conditions stated.

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APPENDIX B

COST ESTIMATE OF DUAL TEST POSITION

FLUORINE TEST FACILITY

TYPE FACILITY	FLUORINE	CONVENTIONAL
1. General Site Development:		
a. Clearing and Grubbing	$ 20,800	$ 20,000
b. Structural Excavation	553,520	353,520
c. Unclassified Excavation	410,000	360,000
Subtotal:	$ 984,320	$ 733,520
2. Test Stands and/or Scrubbers:	$1,732,000	$1,290,000
3. Instrumentation and Control Facilities:		
a. Building	$ 395,000	$ 395,000
b. Tunnels, Cable Trays, etc.	298,500	298,500
c. Conductors	140,000	140,000
d. Instrumentation and Equipment	1,175,000	1,175,000
e. Weather Station Equipment	9,000	----
Subtotal:	$2,017,500	$2,008,500
4. Propellant Storage and Transfer Facilities:		
a. Oxidizer Storage	$ 905,000	$ 600,000
b. Oxidizer Transfer	1,117,600	400,000
c. Fuel Storage	115,370	115,370
d. Fuel Transfer	307,250	307,250
e. Miscellaneous	25,000	25,000
Subtotal:	$2,470,220	$1,447,620

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COST ESTIMATE (Continued)

TYPE FACILITY	FLUORINE	CONVENTIONAL
5. High Pressure Storage and Transfer Area:		
a. Storage Area	$ 445,000	$ 445,000
b. Nitrogen Transfer	178,500	178,500
c. Helium Transfer	229,000	229,000
d. Miscellaneous	10,500	10,500
Subtotal:	$ 863,000	$ 863,000
6. Hydrogen Fluorine Absorption System:		
a. Intake Spray System	$ 7,180	
b. Jet Wheel Manifold	18,800	
c. Scrubber Sprays and Manifold	147,000	
d. Scrubber Duct and Stack	107,000	
Subtotal:	$ 279,980	
7. Water Treatment System:		
a. Water Treatment Tanks	$ 24,660	
b. Collection Basin Water Pump	4,300	
c. Treated Water Pump	3,820	
d. Track Hopper	24,790	
e. Belt Conveyor	3,290	
f. Lime Feeder	490	
g. Bucket Elevator	9,250	
h. Water Reservoir	82,000	
i. Collection Basin	118,520	
j. Settling Ponds	97,940	
k. Lime Silo	5,500	
Subtotal:	$ 374,420	
8. Propellant Dump System:		
a. Fuel Dump Tank	$ 1,660	
b. Fuel Return Pump	710	
c. Fluorine Dump Tank	187,100	
Subtotal:	$ 189,470	

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COST ESTIMATE (Continued)

TYPE FACILITY	FLUORINE	CONVENTIONAL
9. Missile Deluge System:		
a. Ammonia Compressor	$ 1,670	
b. Ammonia Line Mixer	730	
c. Water Pump	820	
d. Ammonia Solution Storage Tank	21,370	
e. Anhydrous Ammonia Storage Tank	9,110	
f. Engine Washdown Pump	10,750	
g. Engine Deluge Pump	23,790	
h. Propellant Tank Deluge Pump	21,570	
i. Missile Deluge Spray System	75,980	
Subtotal:	$ 165,790	
10. Water Distribution System:		
a. Supply to Site	$ 438,320	$ 338,320
b. Potable Storage Tank	20,960	20,960
c. Piping Valves	600,810	250,000
d. Accessories	3,000	1,500
Subtotal:	$1,063,090	$ 610,780
11. Electrical Distribution System:		
a. 12.4 KV Feeder	$ 71,230	$ 71,230
b. Substation and Distribution	133,640	103,640
Subtotal:	$ 204,870	$ 174,870
12. Miscellaneous:		
a. Shop Buildings	$ 82,320	$ 82,320
b. Railroad	368,000	368,000
c. Pavement and Drainage	296,850	296,850
d. Observation Camera Posts	30,000	30,000
e. Burning Pits	25,000	25,000
Subtotal:	$ 802,170	$ 802,170
Total Net Cost:	$11,146,830	$7,930,460
Unforeseen Cost - 10%:	1,114,683	793,046
TOTAL COST:	$12,261,513	$8,723,506

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APPENDIX C

ATMOSPHERIC DIFFUSION

The gaseous HF escaping from the scrubber will be carried by the atmosphere so that the concentration at a downwind point on the ground is given by:

$$C = \frac{2M}{\pi c_y c_z U X^{2-n}}$$

where:

C = Downwind concentration

C_y = Coefficient of lateral dispersion

C_z = Coefficient of vertical dispersion

M = Mass of material emitted per unit time

n = Coefficient of stability

U = Average wind speed

X = Distance downwind from source

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	HIGH ENERGY PROPELLANT MISSILE	CONVENTIONAL PROPELLANT MISSILE
SPECIFIC THRUST (seconds)	275	250
AVERAGE THRUST (pounds)	165,000	360,000
AVERAGE PROPELLANT FLOW RATE (lbs/sec)	600	1,400
MAXIMUM TOTAL DRAG (pounds)	7,500	22,000
MISSILE DIAMETER (feet)	8	12
TOTAL MISSILE WEIGHT (pounds)	113,100	242,900

WHERE BOTH MISSILES HAVE THE FOLLOWING IN COMMON:

MISSILE LENGTH .... 100 FEET
BURNOUT ALTITUDE .... 560,000 FEET
BURNOUT VELOCITY 13,800 FT PER SEC
BURNOUT ACCELERATION .... 625 FT PER SEC/SEC
BURNOUT TIME .... 155 SEC
PAYLOAD ... . 1,500 POUNDS

FIGURE 1

HIGH ENERGY *Versus* CONVENTIONAL
PROPELLANT PERFORMANCE

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OVERALL FLUORINE FACILITY
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FIGURE 2

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FLUORINE SYSTEM FLOW DIAGRAM

FIGURE 3

NATURAL GAS BURNER

LF 50,000 GAL.

LN REFRIGERANT

LF 50,000 GAL.

LF 5,000 GAL.

FUEL

LF 12,500 GAL.

100,000 PD THRUST

HELIUM 70,000 SCF

PRESSURIZES LF STORAGE & MISSLE

NITROGEN 10,000 SCF

LEAK CHECKS BY PRESSURIZATION

LF RAILROAD TANK CAR 5,000 GAL.

VACUUM PUMP

FLUORINE IS HELD LIQUID BY LN REFRIGERANT & VACUUM INSULATION.

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WATER SYSTEM FLOW DIAGRAM

FIGURE 4

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TREATED WATER RESERVOIR 2,000,000 GAL.

WATER 200,000 GAL.

ANHYDROUS AMMONIA 14,000 GAL.

125 TONS LIME

AGITATOR

15,000 GAL TREATMENT TANK

1,000 GPM TRANSFER PUMP

180,000 GAL SETTLING POND

1,000 GPM TRANSFER PUMP

DILUTED HYDROFLUORIC ACID CATCH BASIN 1,000,000 GAL.

1,000 GPM WATER WELL PUMP

54,000 GPM

15 SPRAY TANKS 36-100 GPM NOZZLES PER BANK

36,000 GPM

2,000 GPM ENTRAINMENT NOZZLES

14,000 GPM JET WHEELS IN 2 LEVELS

FOR CORE COOLING ROCKET EXHAUST FLAME

20,000 GPM FILM COOLED FLAME DEFLECTOR

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Lieberman and Marshall

WATER TO 15 WATER SPRAY BANKS
36—100 GPM NOZZLES PER BANK

TO ENTRAINMENT NOZZLE, JET WHEELS,
AND FLAME DEFLECTOR.

WATER HEADER AND JETS ENTRAINMENT
OF BACKUP GASES. 20 JETS AT 100 GPM
EACH.

JACK UP GASES
CONTAINER SHIELD

14,000 GPM
2 LEVEL
JET WHEELS

REDWOOD BAFFLE

MESH DEMISTER

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WATER FROM 2,000,000 GAL
RESERVOIR.

60'

60'

BAFFLES IN
CENTRIFUGAL
STACK.

150'

A

A

30'

30'

BLOW OUT LIDS FOR
EXPLOSIONS

SECTION AA
TYPICAL SPRAY BANK

FIGURE 5

ROCKET EXHAUST GAS DEFLECTOR
AND SCRUBBER

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ASSUMED:

TURBULENT CONDITIONS
$n = 0.20$
$C_y = 0.47$
$C_z = 0.33$
WIND = 10 mph

TEST EMISSIONS = 14 lb per sec.
EQUIVALENT TO 100,000 lb THRUST
SCRUBBER WITH 95% ABSORPTION
OF TOXIC EXHAUST GASES.

FIG. 6
SUTTON EQUATION CALCULATIONS,
DOWNWIND CONCENTRATIONS OF HIGH ENERGY TEST EFFLUENTS

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